ACYCLIC DIENE METATHESIS, A NEW EQUILIBRIUM STEP PROPAGATION, CONDENSATION POLYMERIZATION

By

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Opgedra aan my huisgesin,

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Major Department: Chemistry

The first high molecular weight polymers synthesized by acyclic diene metathesis (ADMET) polymerization are reported herein. Prior to the research discussed in this dissertation, the catalyst requirements and the reaction conditions required to produce high molecular weight polymers by acyclic diene metathesis polymerization techniques were unknown. Thus, this reaction becomes one of only three room temperature step polymerizations known today.

Model compound studies were investigated to eliminate all competing side reactions. The metathesis of styrene, catalyzed by a Lewis acid free catalyst under bulk and high vacuum reaction conditions, yielded stilbene quantitatively, without any traces of side reactions. Substituted styrenes also metathesized cleanly and quantitatively.

A series of 1,9-decadiene polymerizations facilitated the direct comparison of products formed by acyclic diene metathesis polymerization with ring opening metathesis polymerization samples. High molecular weight polyoctenamer samples were produced which had a high percentage trans stereochemistry that resulted in high melting points. A prediction of the melting and recrystallization temperatures of 100% trans polyoctenamer was made. The Mark-Houwink-Sakurada constants for polyoctenamer were calculated for the molecular weight range 10^3-10^5.

Since acyclic diene metathesis produces exclusively linear polymers with no branching, ADMET was applied to 1,5-hexadiene and exclusively linear poly-1,4-butadiene resulted, as indicated by the absence of 1,2-vinyl linkage.

The possibility of acyclic diene metathesis (ADMET) cyclization side reactions and the subsequent ring opening metathesis polymerization were studied by mass spectroscopy and size exclusion chromatography. Parent ion peaks corresponding to linear polymer were observed in both the 1,5-hexadiene and 1,9-decadiene polymerizations. The continued presence of ethylene throughout the course of the reaction indicated the condensation nature of ADMET. A polydispersity approaching 2 was obtained for high molecular weight polyoctenamer and polybutadiene samples. Thus, acyclic diene metathesis polymers are formed by a step propagation mechanism.

CHAPTER 1

INTRODUCTION

During the past 20 years, the olefin metathesis reaction has been explored extensively for its ability to create polymers. Principally, the method investigated has been the ring opening metathesis polymerization (ROMP) of strained cycloalkenes, and as a result several polymers presently are produced commercially using ROMP chemistry [1]. Ring opening metathesis polymerizations are driven by the release of ring strain, and thus ring opening metathesis is limited to the polymerization of strained alkene rings [2].

The polymerization of acyclic dienes has been attempted as well, but with little success prior to the research reported herein [3]. This dissertation reports the first successful metathesis reactions in the equilibrium step propagation condensation polymerization of acyclic dienes, thereby broadening the scope of metathesis polymerization. A variety of acyclic dienes exist that could become monomers for acyclic diene metathesis polymerizations, producing new and unique polymers.

The Nature of Step Polymerization Chemistry

As the name implies, step polymerization proceed in a step-wise manner [4]. Initially, monomer reacts with monomer to produce a dimer, and the dimer can react, in turn, with monomer or another dimer to form either a trimer or tetramer. The step-wise mechanism by which a polymer is progressively formed is illustrated in Figure 1-1.

monomer + monomer $\rightleftharpoons$ dimer
dimer + monomer $\rightleftharpoons$ trimer
dimer + dimer $\rightleftharpoons$ tetramer
trimer + monomer $\rightleftharpoons$ tetramer
trimer + dimer $\rightleftharpoons$ pentamer
trimer + trimer $\rightleftharpoons$ hexamer
etc.

Figure 1-1. Equilibrium step polymerization growth

Monomer disappears early in step propagation reactions, and a range of molecular weight oligomers and polymer chains result. The step-wise growth of monomer to oligomers, eventually reaching high molecular weight polymers, imparts stringent requirements for any chemical reaction to be used in an equilibrium step polymerization [5].

In general, for a small-molecule reaction to be useful in a step polymerization reaction, a favorable equilibrium is necessary. The formation of unstrained rings, as opposed to linear polymer, is an example of an unfavorable equilibrium reaction that can prevent acyclic diene metathesis polymerization.

High conversion (i.e., extent of reaction) is one of the more important criteria required for the synthesis of high molecular weight polymer by step polymerization chemistry. In small molecule synthesis, the reaction is considered to be a success if 90% conversion is achieved. In contrast, a conversion greater than 99% is needed for any step polymerization to produce high molecular weight polymer.

W.H. Carothers [6], derived equation (1) which correlates molecular weight and percentage conversion.

$$\overline{Xn} = 1/(1-p) \qquad (1)$$

According to Carothers, $\overline{Xn}$ is the number average degree of polymerization, and p is the extent or fraction of conversion of functional group to polymer, illustrating the importance of a high extent of conversion. A perfect balance of stoichiometry is assumed in this relationship, and it can be seen that when p equals 0.9 (corresponding to 90% conversion), the "polymer" which results possesses only 10 repeating units, which is an oligomer, not a polymer. A conversion of 99.5% produces a polymer consisting of 200 repeating units and, depending on the molecular weight of the repeating unit, a moderate molecular weight. A step condensation reaction only produces high molecular weight polymer when a high extent of conversion is achieved. Figure 1-2 portrays the relationship between the extent of conversion and the molecular weight of polymer. Chemical reactions that are useful for step polymerizations include esterification, amidation, the formation of urethanes, aromatic substitution and only a few others [4].

p	$\bar{X}_n$
0.8	5
0.9	10
0.95	20
0.99	100
0.995	200

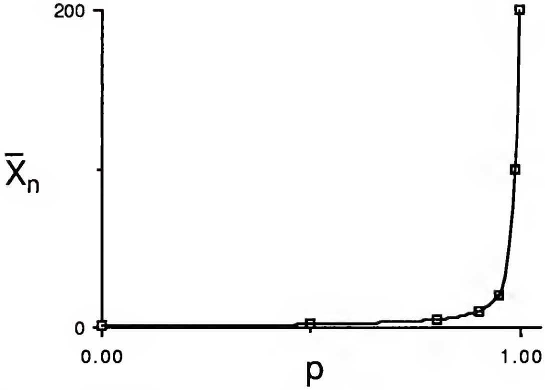


Figure 1-2. Variation of molecular weight with conversion for equilibrium step polymerizations

Two general types of monomers can be employed in step polymerizations. The first type of monomer has two different bifunctional and/or polyfunctional groups with each monomer possessing only one type of functional group. The second type has a single bifunctional monomer containing two different functional groups.or the same monomer. The two groups of reactions can be represented by the following equations, where A and B are the two different types of functional groups.

$$n\ \mathrm{A{-}A} + n\ \mathrm{B{-}B} \rightleftharpoons \left[\mathrm{A{-}AB{-}B}\right]_n \tag{2}$$

$$n\ \mathrm{A{-}B} \rightleftharpoons \left[\mathrm{A{-}B}\right]_n \tag{3}$$

Metathesis represents another reaction in addition to those already mentioned that can be employed as a equilibrium step polymerization mechanism. The monomers that would be suitable for this mechanism have double bonds (i.e., enes) as functional groups, represented schematically as A-A. An equilibrium step propagation condensation type polymerization (4) will produce a repeat unit contain an internal olefin (-B-) and a small molecule (C):

$$n\ \text{A—A} \xrightleftharpoons{\text{catalyst}} \left[\text{B}\right]_n + n\ \text{C} \qquad (4)$$

The removal of the by-product (a small molecule) provides the driving force for a productive polymerization reaction.

The Olefin Metathesis Reaction

The word metathesis is derived from the Greek words meta (change) and tithemi (place), and as a grammatical term, it means the transposition of sounds or letters in a word [7]. For chemistry, metathesis corresponds to the interchange of atoms between two molecules. Olefin metathesis refers to the interchange of carbon atoms between a pair of double bonds (olefins).

Olefin metathesis reactions (Figure 1-3) fall into three broad categories: exchange (5), ring opening polymerization (ROMP) (6), and cyclization reactions (7).

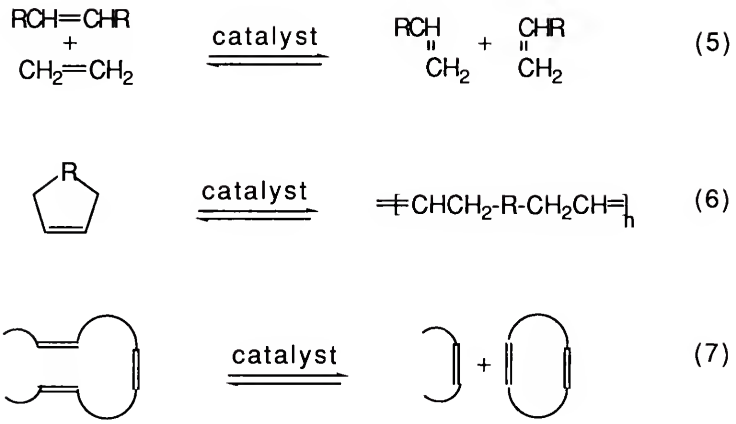


Figure 1-3. Olefin metathesis reactions.

Acyclic diene metathesis (ADMET) polymerization (Figure 1-4) provides the possibility of extending exchange olefin metathesis reactions into a polymerization scheme. Demonstrating the feasibility of employing exchange olefin metathesis as an equilibrium step condensation type polymerization has been the goal of this investigative effort.

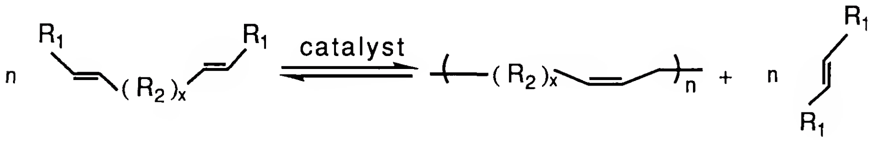
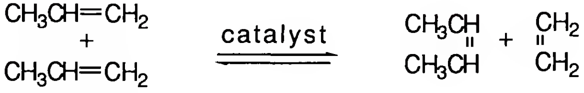


Figure 1-4. The acyclic diene metathesis polymerization reaction.

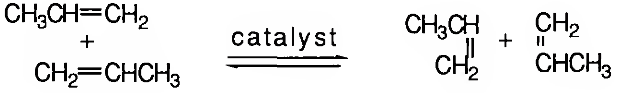
Metathesis reactions generally are reversible, and with an effective catalyst system, an equilibrium can be obtained in a relatively short time. The reversibility of the olefin metathesis reaction results in either a productive or degenerate metathesis product. A productive metathesis reaction produces two chemically different molecules, and a specific example of such a reaction is shown in Figure 1-5, where propene produces 2-butene and ethylene.



$$\begin{array}{c} CH_3CH{=}CH_2 \\ + \\ CH_3CH{=}CH_2 \end{array} \xrightarrow{\text{catalyst}} \begin{array}{c} CH_3CH \\ \| \\ CH_3CH \end{array} + \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}$$

Figure 1-5. The productive metathesis of propylene.

On the other hand, no new chemical compound results when a degenerate metathesis reaction occurs. Degenerate metathesis is illustrated with a specific example in Figure 1-6: propene is the reagent, and propene is also the resultant product.



$$\begin{array}{c} CH_3CH{=}CH_2 \\ + \\ CH_2{=}CHCH_3 \end{array} \xrightarrow{\text{catalyst}} \begin{array}{c} CH_3CH \\ \| \\ CH_2 \end{array} + \begin{array}{c} CH_2 \\ \| \\ CHCH_3 \end{array}$$

Figure 1-6. The degenerate metathesis of propene.

Isotopic labeling studies have shown that degenerate metathesis is much faster than productive metathesis for terminal olefins [8]. By carefully controlling the reaction conditions and catalyst system, the possibility exists that productive metathesis can become the dominant reaction. Productive metathesis must produce yields of better than 99% for olefin metathesis to become a viable reaction in a polymerization scheme. Obtaining the optimum reaction conditions that lead to productive metathesis is one of the criteria to be met before acyclic diene metathesis reactions can produce a step condensation type polymer.

The principal side reactions that can occur during olefin metathesis are; alkylation, isomerization, cyclization, and addition across the double bond. The following precautions have been found to minimize side reactions [9, 10]:

(i) The proper choice of solvent to suppress alkylation reactions; halogenated solvents such as chlorobenzene are preferred.

(ii) The use of a base to suppress cationic side reactions; alkali metal hydroxides can be added to supported catalysts, and tertiary amines or other polar additives can be added to catalyst systems in solution.

(iii) The careful selection of the order of addition of catalyst, cocatalyst, and substrate; and,

(iv) The use of as low a temperature as possible during the reaction.

Brief History of Olefin Metathesis

A patent disclosure by Eleuterio in 1957 on reaction 5 (Figure 1-3), and the norbornene reaction shown in Figure 1-7 were the first metathesis reactions reported. The first literature published on metathesis polymerizations, in 1960 by Truett, concerned the ring opening polymerization of norbornene to polynorbornene (Figure 1-7) [11].

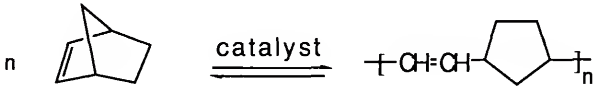
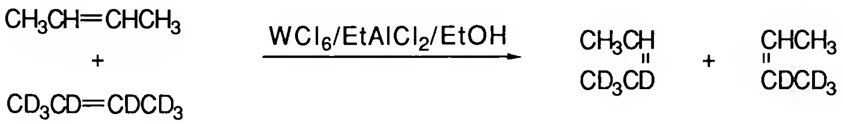


Figure 1-7. The polymerization of norbornene.

Exchange metathesis reactions such as those shown in Figure 1-8 were first published in 1964 by Banks [12].

Calderon, in 1967, coined the expression "olefin metathesis" [13]. Prior to 1967, the chemistry of exchange reactions and of ring opening metathesis polymerization reactions had developed independently. The connection between the two types of reactions was not immediately apparent because different catalysts and conditions were involved.

Calderon's discovery that the catalyst system $WCl_6/EtAlCl_2/EtOH$ would bring about not only the very rapid polymerization of cyclooctene and 1,5-cyclooctadiene [14], but also the disproportionation of 2-pentene [15] at room temperature provided the bridge leading to the realization that olefin disproportionation and ring opening metathesis polymerization were the same chemical reaction. Calderon [16] demonstrated that the double bonds are completely broken in the reaction (Figure 1-8) and lead to the exchange of alkyldiene moieties.



$$\begin{matrix} CH_3CH{=}CHCH_3 \\ + \\ CD_3CD{=}CDCD_3 \end{matrix} \xrightarrow{WCl_6/EtAlCl_2/EtOH} \begin{matrix} CH_3CH \\ \| \\ CD_3CD \end{matrix} + \begin{matrix} CHCH_3 \\ \| \\ CDCD_3 \end{matrix}$$

Figure 1-8. Metathesis reaction illustrating the exchange of alkyldiene moieties.

Consequently, transalkylidenation reactions became known as olefin metathesis reactions. Mol [17], Levisalles [18] and K. Tanaka [19] separately confirmed Calderon's findings, but used isotopically labelled samples with different catalyst systems. Dall'Asta [20] proved that the double bond is completely broken during ring opening metathesis polymerizations of cycloalkenes.

Chemists were quite impressed by the beauty and elegance of the olefin metathesis reaction. Earlier authors frequently used the words, "fascinating, intriguing, exciting and even doubly exciting (commercially and academically)" to describe these reactions. K. J. Ivin [21] wrote about olefin metathesis, "We now know quite a lot about this beautiful woman (metathesis) but she still has a few secrets locked away".

One of those hidden secrets, Acyclic Diene Metathesis Polymerization (ADMET polymerization), has been uncovered by the research reported herein. The beauty and elegance of ADMET polymerizations will be discussed in subsequent chapters.

The Mechanism of Metathesis Chemistry

Originally, metathesis was [22] thought to occur when two double bonds approached one another in the vicinity of the transition metal catalyst site. Transition metal orbitals were proposed to overlap with olefin double bonds to allow exchange to occur via a weakly held cyclobutane type complex. This "pairwise mechanism" (Figure 1-9) has been discarded in favor of the metal carbene chain mechanism [23].

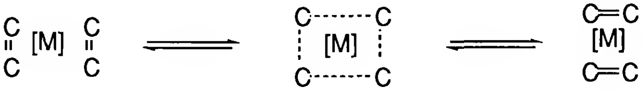


Figure 1-9. The pairwise mechanism.

Herisson and Chauvin first proposed that a metal carbene species might be involved in olefin metathesis [24]. The research describing the initial products of cross metathesis of cyclo- and acyclic olefins, and the identification of both initiating and propagating metal carbenes by ^{1}H and ^{13}C NMR spectroscopy [25, 26, 27, 28] (between 1979 and 1982), is regarded as unequivocal proof of the metal carbene mechanism. Numerous experiments have confirmed the metal carbene mechanism, and it is generally accepted for olefin metathesis reactions. In the metal carbene chain mechanism, the propagating compound is a metal carbene formed in some way from the catalyst/substrate system. Generalized propagating steps are shown in Figure 1-10, where

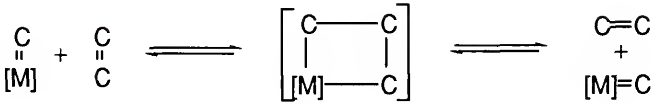


Figure 1-10. The metal carbene mechanism.

propagation proceeds via a metallacyclobutane species. During the process a metal carbene is regenerated at every stage.

Catalysts Used In Olefin Metathesis

Numerous catalyst systems exist that will initiate olefin metathesis reactions. Currently, several researchers [28, 29, 30] are actively pursuing catalytic reactions in search of yet more reactive and better defined organometallic complexes. Metathesis catalyst systems can be divided into three types:

(a) those consisting of an actual metal carbene;

(b) those containing an alkyl or allyl group in one of the components, e.g. $EtAlCl_2$, from which a carbene ligand can readily be generated; and,

(c) those having neither a preformed carbene nor an alkyl group in any component. In this case, a metal carbene can only formed by interaction of the substrate olefin with the transition metal center.

Eleven transition metals are the most commonly used as catalysts: Ti, Zr, Hf, Nb, Ta, Mo, W, Re, Ru, Os and Ir. Compounds containing non-transition metals are not commonly used as a catalyst, with Al_2O_3 [31] and $EtAlCl_2$ [32] being two rare examples.

The metathesis of acyclic olefins is usually thermoneutral. Therefore, if an equilibrium is to be obtained quickly, only the most active Mo-, W-, Re- and Ta- based systems should be used.

A cocatalyst normally consists of an organometallic compound of a non-transition metal from groups I-IV, and the function of the cocatalyst may be severalfold. The cocatalyst may provide an alkyl ligand to the transition metal that can be converted into an alkyldiene ligand. Alternately, the cocatalyst itself may act as a ligand and thereby modify the electron density of the transition metal atom. Presently, much emphasis has been placed on catalyst systems which consist of an actual metal carbene and do not require cocatalysts or activators [28, 29].

Ring Opening Metathesis Polymerization (ROMP).

Eleuterio's (1957) and Truett's (1960) norbornene polymerization disclosures were the first ring opening metathesis reactions performed. These were followed by Natta and Dall'Asta (1964), who reported the metathesis polymerization of cyclopentene using a transition metal catalyst system [33]. Since that time there have been numerous reports of successful polymerizations of cyclic olefins [34-46], and as stated previously, the ring opening metathesis polymerizations (Figure 1-11) are driven by the release of ring strain.

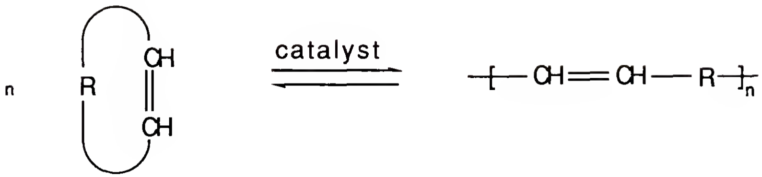


Figure 1-11. Ring opening metathesis polymerization (ROMP).

Schrock, Grubbs, and Osborn investigations have resulted in new metathesis catalysts that are broadening the scope of ring opening metathesis polymerization [28, 29, 30]. The ring opening metathesis polymerization (ROMP) of strained cycloolefins has been the only metathesis reaction leading to the formation of useful polymers. Polyoctenamer [47] (formed from cyclooctene, marketed in 1980) and polynorbornene [48, 49] (formed from norbornene, marketed in 1976) are examples of ring opened polymers that are commercially available.

Extensive research has been done on ring opening metathesis polymerization reactions, and researchers are actively pursuing ROMP chemistry [1]. The effects of ring size, substituents on rings, formation of cyclic oligomers and several other aspects of ROMP reactions have been investigated thoroughly. The use of monocyclic, bicyclic, and tricyclic alkenes as monomers have also been studied [50], and copolymers of cycloalkenes and cross metathesis telomers, formed between cyclic and acyclic olefins were also investigated [51].

Recent studies have revealed, in certain cases at least, that ring opening metathesis polymerization is a living polymerization reaction, and polyuniformities approaching the ideal value of 1.0 have been found [34, 42]. A uniformities of 1.0 demonstrates that the catalyst does not dissociate from the living-chain end and can lead to the formation of block copolymers. However, ring opening metathesis polymerization chemistry is hampered by the fact that monomers are restricted to strained cyclic olefins.

Acyclic Diene Metathesis Polymerization (ADMET)

Acyclic diene metathesis polymerization (ADMET) (Figure 1-4) presents another opportunity to exploit the metathesis reaction to create polymers. Acyclic diene metathesis polymerization is completely different from ring opening metathesis polymerization and offers possibilities not available when one is constrained to cyclic monomers.

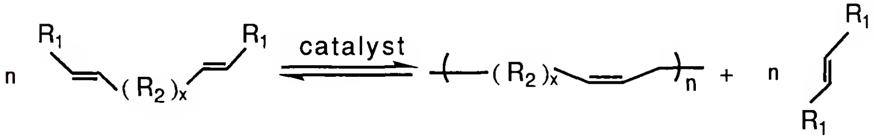


Figure 1-4. Acyclic diene metathesis polymerization (ADMET).

The metathesis reaction of acyclic dienes is an equilibrium reaction that generally has an overall change in free energy close to zero. Reactions do not proceed to high molecular weight polymer, and only oligomers are formed if the equilibrium is not shifted in favor of the forward reaction. Removing the byproduct (small molecule) provides an opportunity to shift the equilibrium and drive the polymerization to high molecular weight.

Side reactions (e.g. the formation of cyclic compounds as opposed to linear products) also limit equilibrium step condensation polymerization reactions [52]. It is especially true for step condensation reactions in which the cyclic product formed is more stable than the linear product and thus becomes the principal product of the reaction. The percentage conversion of monomer to polymer is reduced by cyclization reactions, and according to the Carothers equation (1), only low molecular weight oligomers can be expected [5, 6].

Early studies show that six membered rings are preferentially formed from acyclic dienes where double bonds are separated by four carbon atoms [53]. For example, cis,cis-2,8-decadiene produces cyclohexene in 90% yields.

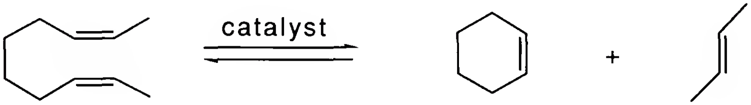


Figure 1-13. The formation of cyclic compounds via acyclic diene metathesis chemistry.

Researchers studied the metathesis reaction of 1,7-octadiene [49] to gain insight into the mechanism of metathesis. Several catalyst systems were used, and without exception the products are cyclohexene and small quantities of oligomers.

Reactions with isotopically labeled terminal olefins revealed that degenerate metathesis is much faster than productive metathesis [8]. Subsequently, degenerate metathesis explains the fact that for acyclic dienes, without exception, only oligomers are formed under the reaction conditions employed. One reaction that received significant attention was the attempted acyclic diene metathesis polymerization of 1,5-hexadiene to polybutadiene [54, 55]. It was eventually concluded that ADMET polymerization of 1,5-hexadiene was impossible because degenerate metathesis is strongly favoured [56].

By the late 1970s it was generally accepted that acyclic dienes would not produce linear polymers by acyclic diene metathesis. What would have been the first new step condensation type polymerization reaction in 20 years was abandoned, and polymerization efforts were focused on ring opening metathesis polymerization reactions.

This dissertation demonstrates unequivocally that acyclic diene metathesis (ADMET) polymerization is possible. It elaborates on the requirements necessary for acyclic diene metathesis to become a feasible polymerization reaction. Specific model compound studies were performed to gain insight regarding the requirements necessary for acyclic diene metathesis to be used as a polymerization reaction. Two important polymers were prepared by acyclic diene metathesis polymerizations and reaction conditions and the properties of the formed polymers were delineated.

CHAPTER 2
EXPERIMENTAL

General Information

A Varian XL-Series NMR Superconducting Spectrometer system was used to obtaine ^1H NMR 200 MHz and ^{13}C NMR 50 MHz spectra. Chemical shifts are reported in parts per million downfield from the internal reference tetramethylsilane. Infrared spectral analysis was performed on a Perkin-Elmer 281 Infrared Spectrophotometer with KBr pellets and percent transmission being recorded relative to wavenumber. Ulraviolet spectroscopy was done with a Perkin-Elmer Lambda 9 UV/Vis/NIR spectrometer using THF as solvent. Elemental analyses were done by Atlantic Microlab inc. in Norcross, Georgia. Mass Spectroscopic data were obtained from a Finnigan 4600 Gas Chromatographic Mass Spectrometer. Differential scanning calorimetry data were obtained with the Perkin-Elmer 7 Series Therm Analysis system, equipped with a data station. The instrument was calibrated by a two point method using cyclohexane and indium. Dry argon was used as purge gas, and a scan rate of 10°C per minute was used.

Size exclusion chromatograph data was obtained using a Waters Associates Liquid Chromatograph apparatus equipped with an RI detector. Tetrahydrofuran or toluene were used as solvent and μstyragel columns covering the region of interest were employed. A constant flow rate of 1.04 ml/min was maintained and the instrument calibrated by using polybutadiene or polystyrene standards (Polysciences, Inc.) that covered the region of interest. Intrinsic viscosities were determined using an Oswaltd dilution viscometer at 25 °C with toluene as the solvent. A Wescan Vapor Pressure Osmometer model 233 was used for osmometry. Toluene was the solvent of choice at an operating temperature of 51°C.

High Vacuum and Schlenk Line Techniques

The catalysts used for metathesis reactions vary in their sensitivity toward impurities, such as moisture and oxygen[57]. Since little is known about the exact conditions required for metathesis to occur when vinyl bonds are used, a variety of reaction conditions were employed to optimize the synthesis of model compounds, and polymers.

Schlenk Vacuum Line Techniques

The first polymerizations of 1,9-decadiene and 1,5-hexadiene were carried out with a Lewis acid containing catalyst system ($WCL_6/ETAlCl_2$) using Schlenk line techniques [58]. Schlenk techniques also were used initially in the model compound studies. A specially designed flask (Figure 2-1) equipped with a porthole having a Suba Seal™ rubber septum and a ground glass joint (14/20) was designed, and the ground glass joint was connected to a gas trap in the system. All condensed gases were analyzed with a gas chromatography equipped with a flame ionization detector, or a

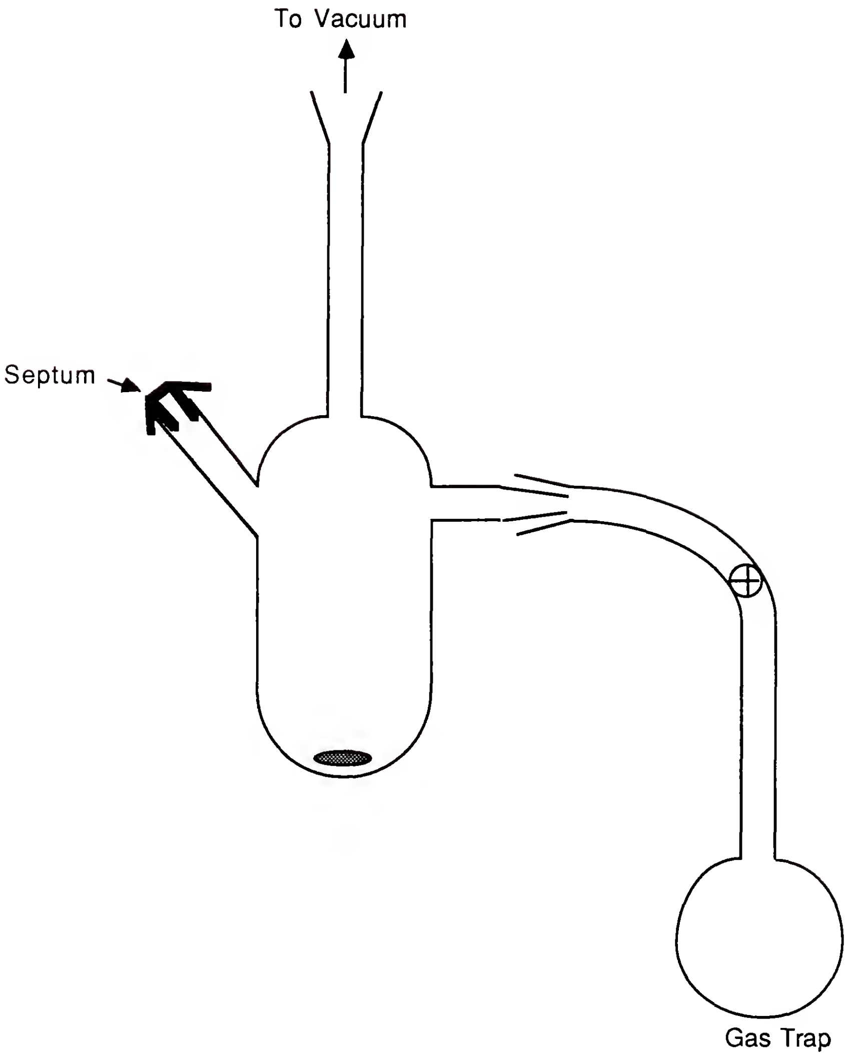


Figure 2-1. Schlenk vacuum line apparatus

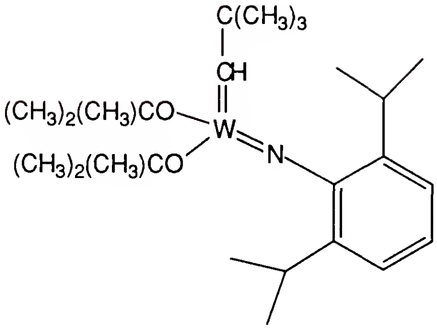
mass spectrometer.

In a typical experiment, freshly sublimed tungsten hexachloride (WCl_6) was added into the flask described above, which was placed in a dry box free of oxygen and moisture. When chlorobenzene was used as solvent, a 1.0 M solution of WCl_6 in chlorobenzene was used instead of powderous WCl_6. The flask was sealed using a septum and a Rotaflo™ stopcock. This apparatus was connected to a Schlenk vacuum line via a ground glass joint and then evacuated. The gastrap of the apparatus was closed off from the vacuum line using an in-line Rotaflo™ stopcock, and the system was filled with dry argon. The reagent and the co-catalyst were added via a syringe.

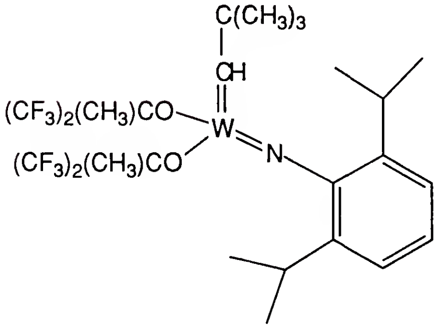
Schlenk methods allowed for the addition of reagents in varying order and quantities. The gas trap was cooled in liquid nitrogen while the reaction mixture was chilled in an ice bath. A moderate vacuum was applied to the system by opening the Rotaflo™ joint of the gas trap, and the condensed gases were removed for further analysis.

High Vacuum Line Techniques

Due to the high oxygen and moisture sensitivity of the Lewis acid free catalyst system (Catalyst 2; $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$, Figure 2-2), high vacuum line techniques had to be employed when this catalyst was used. A vacuum system, custom-made in the University of Florida glass shop [59], was constructed entirely of Pyrex™ glass and consisted of a rotary oil pump in conjunction with an oil diffusion pump. High vacuum Pyrex™



Catalyst 1



Catalyst 2

Figure 2-2. Lewis acid free catalysts used in metathesis reactions.

ground glass joints were used at various junctions in the line to permit evacuation of reaction vessels and to transfer solvents and reagents from one vessel to another. A mercury McCleod gauge, attached to the manifold, was used to monitor the pressure in the system.

The Pyrex™ glass vessels used in the reactions were self designed and built with the use of a hand-held gas and oxygen torch (Figures 2-4, 2-7, 2-8, 2-9 and 2-10). The manipulations required for various reactions, such as catalyst addition and transfer of reagents, were performed in vacua using breakseal techniques [60, 61]. All glassware used was cleaned in the following order: KOH/isopropanol (15% W/V), water and acetone. The apparatus was oven dried before attaching it to the vacuum line. The entire system was evacuated and dried thoroughly with a torch to remove traces of adsorbed water vapor and oxygen from the surface of the glass. The system then was checked for the presence of pinholes using a Tesla high voltage discharge coil. Reactions were carried out only after confirming that a "sticking vacuum" (10^{-6} mm Hg) existed, as registered on the McCleod gauge.

The reactions were terminated by disconnecting the apparatus from the vacuum line and then opening the Rotaflo™ joints, which allowed air into the system to destroy the catalyst. Following these operations, the apparatus had to be cut into smaller sections to remove the products.

Purification of Monomers, Reagents and Solvents

All chemicals were of high grade purity (>98%). Due to the sensitive nature of catalysts 1 and 2 (Figure 2-2), all monomers, reagents and solvents used in conjunction with these catalysts were of greater than 99% purity. In order to ensure absolute dryness and an oxygen free atmosphere, all chemicals used were dried over calcium hydride for 24 hours, degassed several times using freeze-pump-thawing cycles, and then vacuum transferred into a potassium mirrored flask. The reagents were stirred for a half hour and then vacuum transferred into a divider. Break-seals filled with the desired amounts of reagent were frozen in liquid nitrogen and sealed under a 10^{-6} mm Hg vacuum (Figure 2-3).

In cases where a reagent had impurities not removed by drying techniques, the reagent was allowed to react with a single aliquot (20 mg) of catalyst 2 for 15 minutes, then the purified reagent was vacuum transferred into a new breakseal and sealed under high vacuum. Allowing any impurities to react with catalyst (in effect destroying the catalyst) and then removing the remainder of the pure reagent from the reaction vessel, proved effective for removing impurities that would otherwise poison the catalyst and prevent metathesis. Without exception, reagents purified by exposure to catalyst metathesized and produced only the expected products in high yields.

The reagents used with the classical catalyst system, $WCl_6/EtAlCl_2$, were purified in an identical fashion up to the point that they were sealed in breakseal ampules. The reagents were vacuum transferred from the potassium mirrored reaction vessel

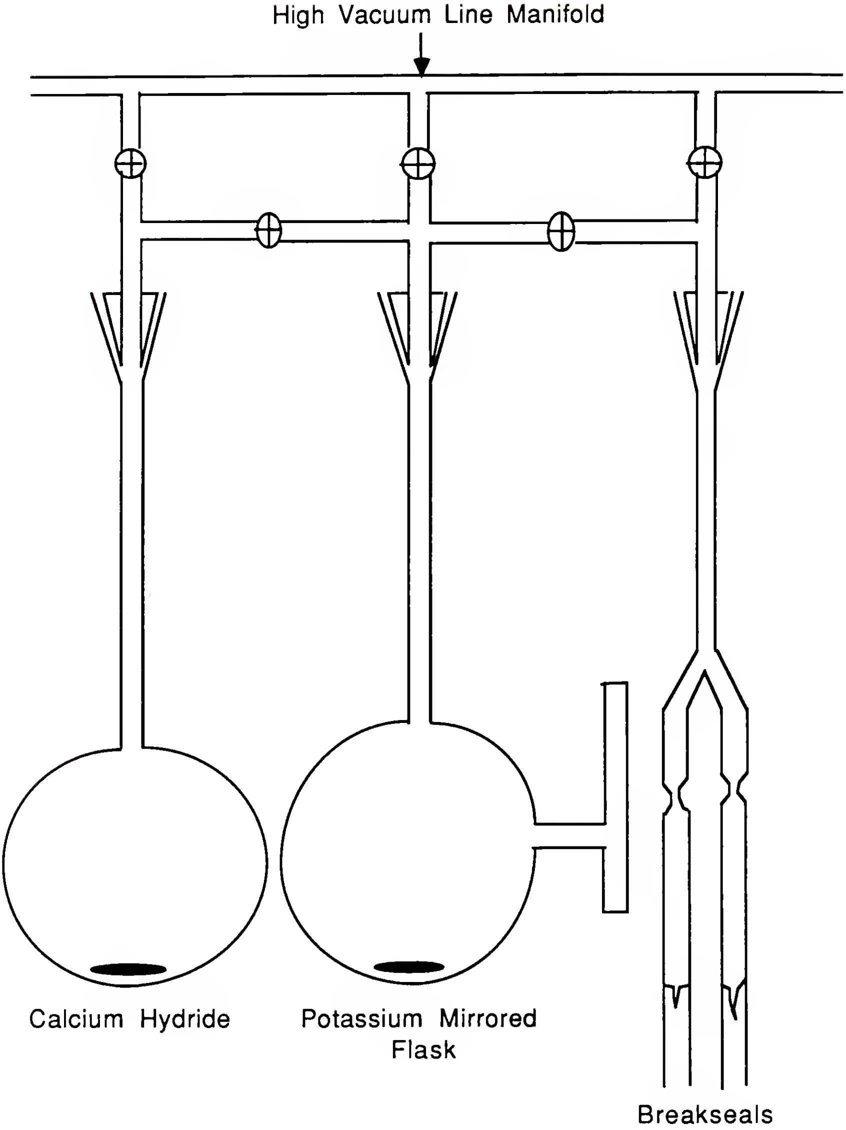


Figure 2-3. High vacuum line purification setup.

into a 50 ml round bottom flask by cooling the flask in a liquid nitrogen bath. After the reagents were allowed to thaw, the flask was filled with argon and sealed with a rubber septum. Storing the reagent under argon in a round bottom flask facilitated the use of Schlenk vacuum line techniques (i.e., transfer through double ended needles under argon).

Attempted Metathesis of Styrene Using a Lewis Acid Containing Catalyst

An attempted model metathesis reaction of styrene to stilbene was conducted repeatedly to determine the reaction conditions and catalyst system which would lead to the expansion of the metathesis reaction into a equilibrium step propagation, condensation type polymerization. The order in which the catalyst, co-catalyst, and styrene were added was varied, as was the time that the catalyst and co-catalyst were allowed to react, particularly when the reagent was added last. The variations were done to investigate the possibility of eliminating side reactions. Styrene generally was added while the apparatus was cooled in an ice bath, after which the reaction was allowed to warm to room temperature. The first reaction was started at -78°C, and once all reagents were added, the reaction was allowed to slowly warm to room temperature. Also, several reactions were started at room temperature. The above variations in reaction conditions were employed using both Schlenk and high vacuum techniques.

Tungsten hexachloride (Aldrich) was stored in a dry box and periodically sublimed in order to ensure purity. Tungsten hexachloride (0.9929g) was dissolved in 25 ml of chlorobenzene to produce a 0.1M solution which was stored in a Schlenk flask under argon. A variety of co-catalysts (i.e., $EtAlCl_2$, Et_2AlCl and Et_3Al) were used as 1.0 M solutions in hexane in separate reactions. The co-catalyst was added to the reaction vessel via a syringe. The ratio of the cocatalyst to WCl_6 was 4:1. Hexane was removed from the reaction vessel and replaced with argon. The apparatus was cooled in an ice-bath, and the reagent was added to the vessel via a syringe through the septum. Typically, 0.82 ml of a 0.1 M WCl_6 (0.082 mmol) in chlorobenzene was used with 1 ml of styrene (9.6 mmol) and 0.33 ml of a 1.0 M $EtAlCl_2$ (0.33 mmol) in hexane. The reactions performed, utilizing the above variations in reaction conditions, were allowed to continue for varying lengths of time and were terminated with an excess of methanol. ^1H and ^{13}C NMR spectra of the products indicated that only polystyrene was produced. The gases produced in these reactions were analyzed at 5-minute intervals by removal of a 50 μl aliquot with a gastight syringe. A mixture of ethane and ethylene, as analyzed by GC/MS, was observed with ethane as the major product. Varying the solvent and the addition sequence of reagents did not produce stilbene.

It was concluded that different reaction conditions had to be utilized to eliminate the side reaction that produced polystyrene and inhibited metathesis. High vacuum techniques were employed. Tungsten hexachloride (0.82 ml of a 0.1 M in chlorobenzene) and $EtAlCl_2$ (0.33 ml of a 1.0 M in hexane), at a ratio of 1:4, were added, in a dry box, into break-seal ampules via a syringe. The break-seal ampules were sealed with rubber septa and then removed from the dry box. After freezing them in liquid nitrogen, a vacuum was applied using a needle pierced through the septum. The break-seal ampules were then sealed under vacuum using a hand held gas and oxygen torch. Styrene (8.6 ml) was purified as described previously and sealed in a break-seal ampule to give a 100:1 mol ratio with respect to WCl_6. The ratio of catalyst: co-catalyst: reagent, typically were 1:4:100.

The break-seal ampules containing the catalyst, co-catalyst and reagent were joined to a reaction vessel (Figure 2-4) and the reaction vessel was connected to the high vacuum line via a ground glass 14/35 joint and evacuated. After closing the gas trap by closing the Rotaflo™ stopcock, the reagents were added in varying order by breaking the break-seal ampules. Hexane (solvent for the co-catalysts) was evacuated after the breakseal containing the co-catalyst was broken. At this point the reaction vessel was sealed off from the vacuum line to prevent any impurities from entering the reaction. By opening the Rotaflo™ stopcock of the gas trap and cooling the trap in liquid nitrogen, a steady vacuum was applied, and any gases produced in the reaction could be removed and condensed. Thus, a constant vacuum used to drive the reactions could be maintained. No gases were produced, and the only product was polystyrene, which was corroborated by the following analysis.

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 41 (methine carbons), 43-46 (methylene carbons), 145-146 (aromatic carbons).

CHN : %C = 92.31, %H = 7.69 (Theory)
%C = 92.29, %H = 7.72 (Found)

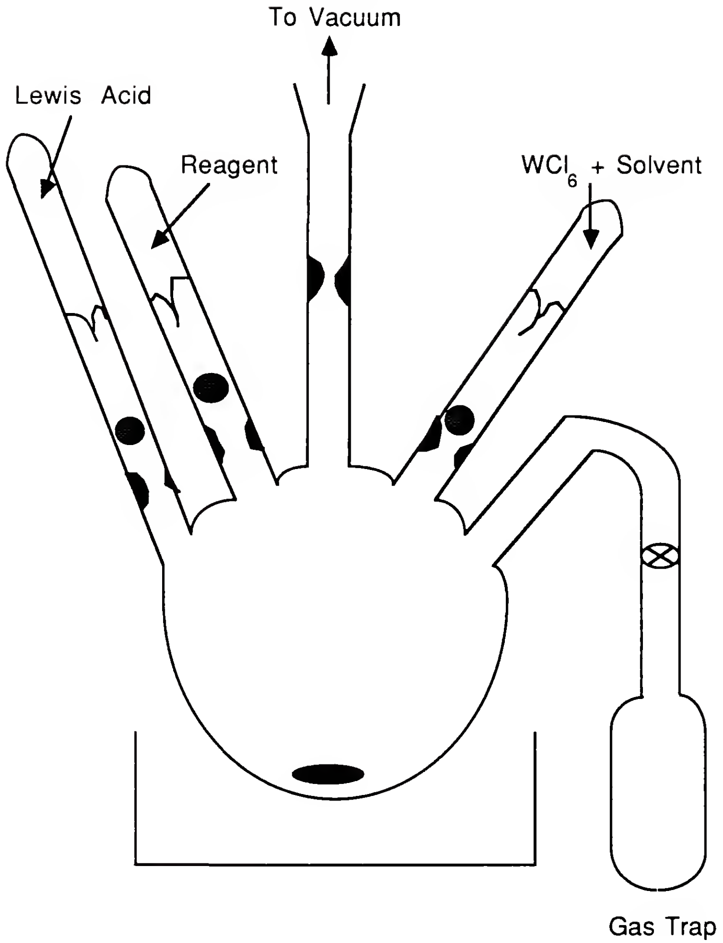


Figure 2-4. High vacuum breakseal apparatus.

Attempted Metathesis of Fluorinated Styrenes Using a Lewis Acid Containing Catalyst System

In order to investigate the possibility of metathesizing fluorinated styrenes, four different fluorinated styrenes were used: 2-fluorostyrene, 3-fluorostyrene, 4-fluorostyrene and 2,3,4,5,6-pentafluorostyrene. The experimental procedures for these reactions were identical to those adopted for the metathesis of styrene. The results also were identical: monofluorinated styrenes produced fluorinated polystyrenes. Authentic fluorinated polystyrenes samples were not available and were subsequently prepared by means of anionic polymerization techniques discussed in the next section of this chapter. Spectral data of fluorinated polystyrenes formed when a Lewis acid cocatalyst is used are:

Poly-2-fluorostyrene

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 35 (methine carbons),40-41 (methylene carbons), 114-129 (aromatic carbons), 131 (substituted aromatic quarternary carbons), 160,5d, $J_{C\text{-}F}$ = 246 Hz (fluorinated aromatic carbons).

Poly-3-fluorostyrene

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 40 (methine carbons), 41-46 (methylene carbons), 113-130 (aromatic carbons), 147 (substituted aromatic quarternary carbons), 162,5d, $J_{C\text{-}F}$ = 243 Hz (fluorinated aromatic carbons).

2,3,4,5,6-Pentafluorostyrene did not react under the reaction conditions described. In order to determine if the catalyst was active, experiments were run in which 1,9-decadiene (shown in this work to metathesize) was added to the reaction of 2,3,4,5,6-

pentafluorostyrene after approximately 24 hours. 1,9-Decadiene (0.5 ml) was syringed into the reaction vessel through the septum after the vessel was filled with argon while using Schlenk vacuum line techniques. 1,9-Decadiene oligomerized, indicating that the catalyst was active.

When high vacuum line techniques were used, 1,9-decadiene again was employed to test for catalyst activity. Under high vacuum conditions, breakseal ampules containing purified 1,9-decadiene (0.5 ml) were incorporated into the reaction vessel prior to the start of the reaction to allow for the addition of 1,9-decadiene at any stage of the reaction. The breakseal ampules were used as a precaution against contamination of the reaction with oxygen or moisture. NMR analysis indicated that 1,9-decadiene oligomerized to polyoctenamer, whereas 2,3,4,5,6-pentafluorostyrene did not metathesize or polymerize. Thus, the catalyst was active but did not cause 2,3,4,5,6-pentafluorostyrene to react.

Preparation of Fluorinated Polystyrene by Anionic Polymerization Techniques

Authentic fluorinated polystyrenes were unavailable for comparison with the products formed when a Lewis acid containing catalyst is reacted with fluorinated styrenes, and so high vacuum line techniques were used to make authentic fluorinated polystyrenes. The apparatus illustrated in Figure 2-5 was used in the preparation of these polymers.

All fluorinated styrene reagents were dried over calcium hydride and then distilled on a vacuum line into a round bottom

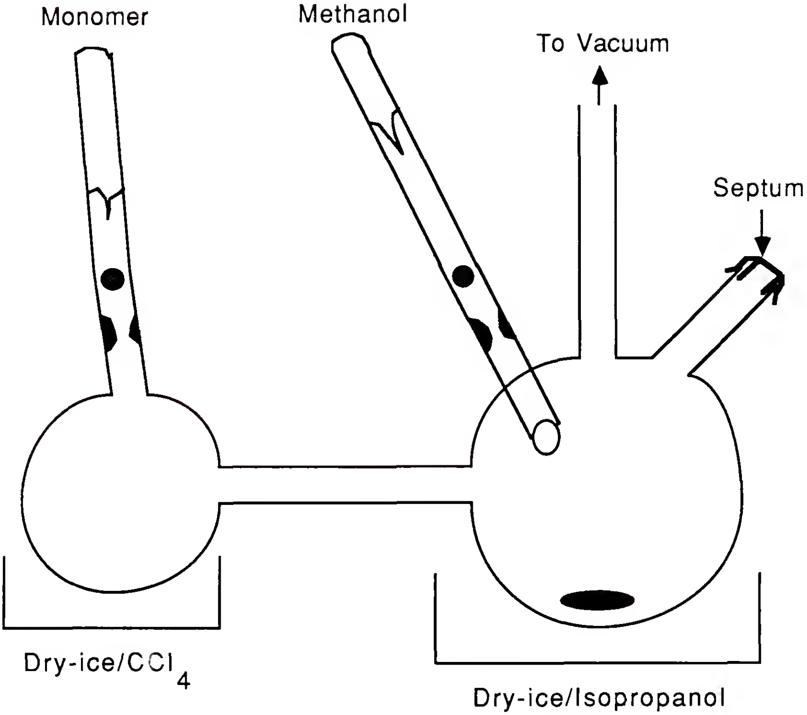


Figure 2-5. Anionic polymerization apparatus.

flask, which was coated with potassium metal. After stirring for 30 minutes the monomer was transferred into a breakseal ampule and sealed under vacuum. Approximately 2 ml of the monomer was sealed in each breakseal ampule and vacuum sealed

The apparatus was connected to the vacuum line, evacuated, flame dried to ensure absolute dryness and then filled with dry argon. One milliliter of a 1.6 molar solution of t-butyllithium, used as the initiator, was syringed into the vessel through the septum. The reaction section of the apparatus was cooled in liquid nitrogen. The whole apparatus was evacuated, after which the sidearm with the septum was sealed off using a gas/oxygen flame. Dry tetrahydrofuran, approximately 50 ml, was distilled into the vessel, and the apparatus was sealed from the vacuum line.

Tetrahydrofuran and t-butyllithium (0.1 ml) were allowed to warm to -78°C and were kept at this temperature in a dry-ice/isopropanol bath. The breakseal ampule containing the fluorinated styrene (5 ml) under study was broken, and the reagent was allowed to flow into the round bottom flask that had been cooled to -20°C using a dry-ice/carbon tetrachloride bath. Addition occurred over a one hour period to facilitate the slow and controlled transfer of the monomer into the reaction section of the apparatus. The reaction was allowed to continue for 2 hours at -78°C and was slowly warmed to room temperature; then stirred for an additional 2 hours. In each case, dry methanol was used to terminate the reaction.

These anionically prepared reference polymers were precipitated using an excess of methanol and further purified by dissolving them in benzene, followed by precipitation in methanol. The NMR spectra of all of these polymers were identical to those of the products formed when a Lewis acid was used as co-catalyst in the metathesis reactions, described previously. These results confirm that fluorinated polystyrenes result when a Lewis acid containing catalyst is reacted with fluorinated styrenes as reagents. Typical data for the polymers are as follows:

Poly-2-fluorostyrene

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 35 (methine carbons), 40-41 (methylene carbons), 114-129 (aromatic carbons), 131 (substituted aromatic quarternary carbons), 160,5d, $J_{C\text{-}F}$ = 246 Hz (fluorinated aromatic carbons).

Poly-3-fluorostyrene

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 40 (methine carbons), 41-46 (methylene carbons), 113-130 (aromatic carbons), 147 (substituted aromatic quarternary carbons), 162,5d, $J_{C\text{-}F}$ = 243Hz (fluorinated aromatic carbons).

Poly-2,3,4,5,6-pentafluorostyrene

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 33 (methine carbons), 37-39 (methylene carbons), 115 (substituted aromatic quarternary carbons), 135.5m, 138m, 140.5m, 143m, 148m (fluorinated aromatic carbons)

Metathesis of Styrene Using a Lewis Acid Free Catalyst

The catalytic ability of a Lewis acid free catalyst was examined using styrene as a model reaction. Styrene (Fisher) was purified by stirring over calcium hydride for 24 hours, followed by fractional distillation under vacuum (75°C/95 mmHg). The middle fraction was collected in a breakseal ampule, and the ampule was attached to the apparatus (Figure 2-6), then evacuated. A side arm containing freshly cut potassium metal was heated gently with a torch to form a shiny mirror in the main flask. The break-seal ampule containing styrene was broken and the styrene was stirred for 30 minutes over the potassium mirror to ensure absolute purity. After degassing, the liquid was distilled into a divider, and the break-seals of each ampule were carefully sealed off and stored in a freezer.

Catalyst 2, $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$, (Figure 2-2, page 22), stored in a dry-box because of its oxygen and moisture sensitivity, was dissolved in pentane (20 mg/2 ml) and transferred to a break-seal ampule via a syringe. The break-seal was then removed from the dry box and sealed under vacuum. Break-seals containing styrene (1.5 ml) and the catalyst (ratio of 500:1) were connected to the apparatus illustrated in Figure 2-7. The apparatus then was connected to the high vacuum line via a 14/35 ground glass joint and evacuated. The entire apparatus was flame dried and the gas trap was closed. The catalyst was introduced into the reaction flask and the solvent (pentane) removed by evacuation, after which the apparatus was sealed off and removed from the line. As soon as styrene was introduced, the vacuum trap was opened and the gasses that were produced were condensed with a liquid nitrogen bath. After approximately 2 hours, the reaction mixture had turned into a light yellow solid, which was determined to be trans stilbene. The product was dissolved in a

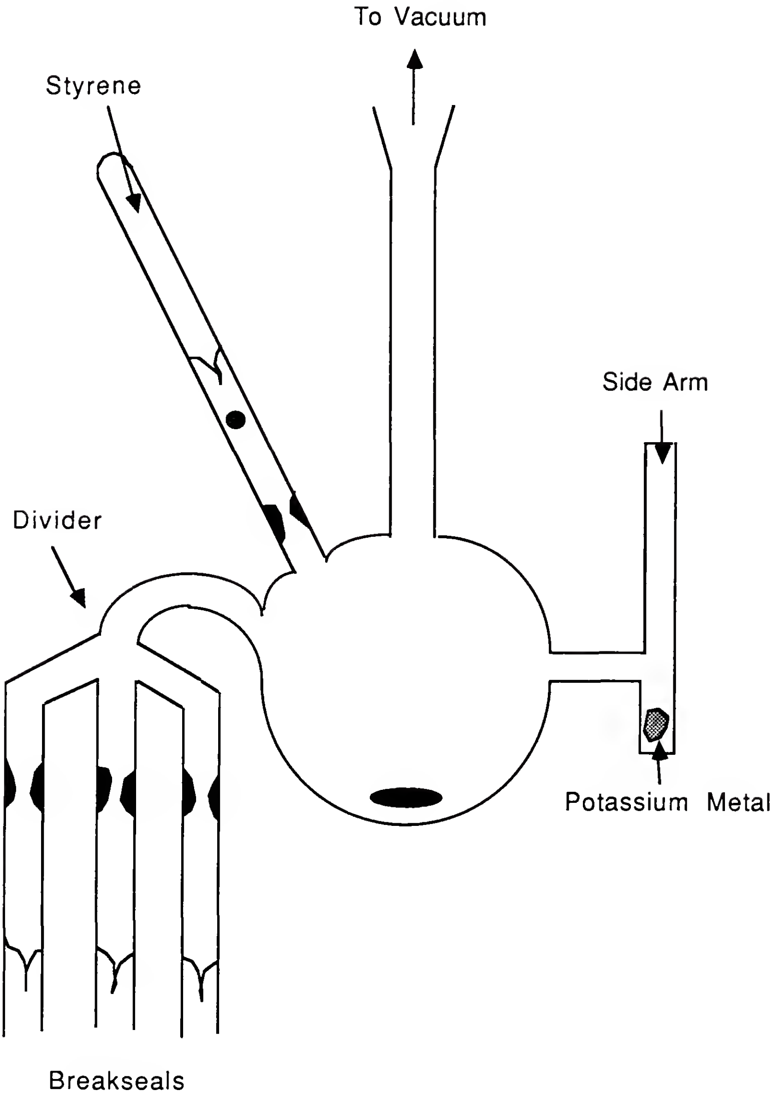


Figure 2-6. Styrene purification over a potassium mirror.

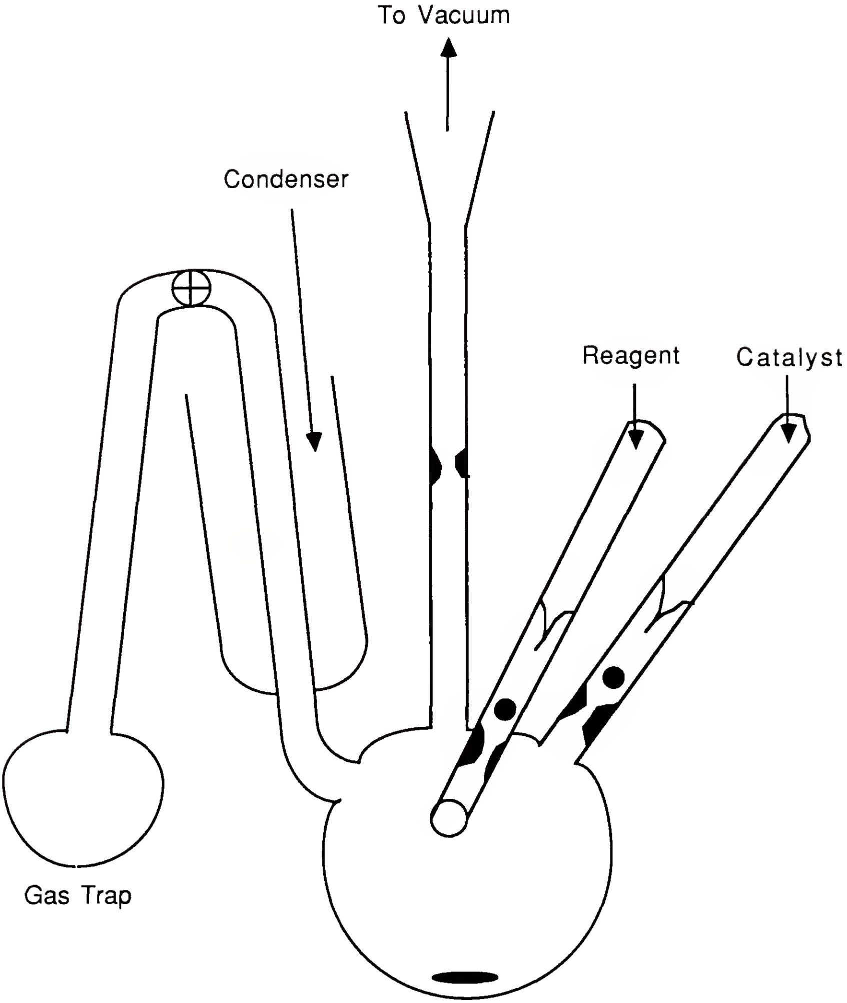


Figure 2-7. Reaction flask for metathesis of various styrene reagents.

minimum amount of hot ether and allowed to precipitate in the freezer. Typical data obtained from these reactions are as follows:

Trans stilbene

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 7.05 (vinyl methine protons), 7.15-7.5 (aromatic protons).

^{13}C NMR ($CDCL_3$, 50 MHz, δ in PPM): 126.4, 127.5 and 128.6 (aromatic carbons), 128.7 (methine carbons), 137.3 (substituted aromatic quarternary carbons).

CHN: %C = 93.3, %H = 6.67 (Theory)
%C = 93.2, %H = 6.62 (Found)

Metathesis of Fluorinated Styrenes Using a Lewis Acid Free Catalyst

The ability of the Lewis acid free catalyst to initiate metathesis on electron deficient vinyl bonds was tested by employing fluorinated styrenes as reagents. 2-Fluorostyrene (Lancaster Synthesis Ltd), 3-fluorostyrene (Lancaster Synthesis Ltd) and 4-fluorostyrene (Lancaster Synthesis Ltd) were all purified and reacted with catalyst 2. The reactions were all conducted in the exact manner as described for styrene i.e., approximately 1.5 ml of reagent was reacted with 20 mg of catalyst 2.

All products were dissolved in hot ether and allowed to precipitate in a freezer. The products of the reaction of 4-fluorostyrene formed long white needle like crystals was determined to be pure 4,4'-difluorostilbene. The data for the product, corroborated by the literature data for 4,4'-fluorostilbene, follows:

^{1}H NMR (CDCl$_3$, 200 MHz, δ in PPM): 6.94 (vinyl methine protons), 6.97-7.46 (aromatic protons)

^{13}C NMR (CDCl$_3$, 50 MHz, δ in PPM): 115,6d, J_{C-F} = 20 Hz, 128,8d, J_{C-F} = 5 Hz (aromatic), 127,2 (vinyl), 133,3d, J_{C-F} =3 Hz (substituted aromatic), 162,3d, J_{C-F} = 245 Hz (fluorinated aromatic).

CHN: %C = 77.77, %H = 4.66 (Theory)
%C = 77.82, %H = 4.72 (Found)

The products of the 2-fluorostyrene reaction and 3-fluorostyrene reaction did not crystallize as well as those from the 4-fluorostyrene reaction. However, the NMR and CHN data, listed below confirm them to be 2,2'-difluorostilbene and 3,3'-difluorostilbene, respectively.

2,2'-Difluorostilbene

^{1}H NMR (CDCl$_3$, 200 MHz, δ in PPM): 7.33 (vinyl methine protons), 7.0-7.3 and 7.58-7.68 (aromatic protons).

^{13}C NMR (CDCl$_3$, 50 MHz, δ in PPM): 115,8d, J_{C-F} = 25 Hz, 122,9, 124,3, 129,1d, J_{C-F} = 8 Hz (aromatic), 127,1 (vinyl), 125,1d, J_{C-F} =10 Hz (substituted aromatic), 160,5d, J_{C-F} = 246 Hz (fluorinated aromatic).

CHN: %C = 77.77, %H = 4.66 (Theory)
%C = 75.51, %H = 5.00 (Found)

3,3'-Difluorostilbene

^{1}H NMR (CDCl$_3$, 200 MHz, δ in PPM): 7.1 (vinyl methine protons), 6.89-7.0 and 7.3-7.34 (aromatic protons)

^{13}C NMR (CDCl$_3$, 50 MHz, δ in PPM): 112,9d, J_{C-F} = 21 Hz, 114,6d, J_{C-F} = 18 Hz, 122,6, 130,0d, J_{C-F} = 10 Hz (aromatic), 128,8 (vinyl), 139,1d, $J_{C\text{-}F}$ =10 Hz (substituted aromatic), 163,2d, $J_{C\text{-}F}$ = 243 Hz (fluorinated aromatic).

CHN: %C = 77.77, %H = 4.66 (Theory)

%C = 77.75, %H = 4.68 (Found)

Metathesis of Substituted Styrenes Using a Lewis Acid Free Catalyst

4-Bromostyrene and 3-methylstyrene were metathesized in the exact manner as for styrene and produced, exclusively, their substituted stilbene analogues. The data obtained were:

4,4'-Dibromostilbene

^1H NMR ($CDCl_3$, 200 MHz, δ in PPM): 7.01 (vinyl methine protons), 7.26-7.5 (aromatic protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 121.6 (aromatic substituted quarternary carbons), 127 and 128 (aromatic carbons), 131.9 (vinyl methine carbons), 135.8 (brominated aromatic carbons).

CHN: %C = 49.73, %H = 2.96 (Theory)

%C = 49.12, %H = 2.55 (Found)

3,3'-dimethylstilbene

^1H NMR ($CDCl_3$, 200 MHz, δ in PPM): 2.34 (methyl protons), 7.05 (vinyl methine protons), 7.1-7.35 (aromatic protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 21.4 (methyl carbons), 123, 127 and 128 (aromatic carbons), 137.3 (substituted aromatic quarternary carbons), 138.0 (methylated aromatic carbons)

CHN: %C = 92.31, %H = 7.69 (Theory)

%C = 86.89, %H = 7.78 (Found)

Acyclic Diene Metathesis (ADMET) Polymerization of 1,9-Decadiene

General Polymerization Procedure.

Several acyclic diene metathesis (ADMET) polymerizations were investigated using a Lewis acid free catalyst and 1,9-decadiene as the monomer. The monomer was dried over calcium hydride, then subjected to four freeze thaw vacuum cycles to remove dissolved gases. To insure absolute dryness, the monomer was transferred in a vacuum line to a flask containing a potassium mirror, where it was stirred for approximately one hour. The purified monomer was transferred under vacuum to breakseal ampules and were sealed under high vacuum.

1,9-Decadiene (Aldrich) was 98% pure (as determined by GC/MS), and the impurities that were not eliminated by the drying techniques just described, were removed by allowing the monomer to react with a single aliquot (20 mg) of catalyst 2 for 15 minutes. The purified monomer was vacuum transferred into new breakseal ampules, then sealed under high vacuum. Allowing impurities to react with the catalyst, in effect destroying a portion of the catalyst, proved to be an effective method to eliminate impurities. Monomers purified by this method, without exception, exclusively metathesized and produced only the expected products in quantitative yields.

Catalyst 2, $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$, was prepared according to published procedures [62, 63]. Twenty mg of catalyst 2 were dissolved in 2 ml pentane and transferred into a breakseal ampule. The transfer was performed in a dry box, in an argon atmosphere, and the breakseal ampule containing the catalyst solution was sealed with a rubber septum and removed from the dry box. After freezing the catalyst solution in liquid nitrogen and applying a high vacuum via a needle pierced through the septum, the breakseal ampule was sealed using a gas/oxygen flame.

Breakseal ampules containing aliquots of the catalyst solution and the purified monomer were connected to a single reaction vessel, which itself was designed specifically to perform these polymerizations. Prior to all polymerizations, the entire apparatus was connected to a high vacuum line and flame dried to remove all traces of oxygen and moisture adsorbed onto the glass.

The first reaction was performed using the apparatus illustrated in Figure 2-7. Solvent (i.e., toluene) could not be added once the reaction was started; thus, the apparatus had to be modified.

A new apparatus (Figure 2-8) subsequently was designed which allowed for the removal of ethylene by opening Rotaflo™ stopcock A. However, this apparatus produced only oligomers due to the precipitation of the reaction product in the breakseal connection arms and was not used further.

This precipitation in the breakseals was eliminated by placing the breakseals above the condenser (Figure 2-9). The apparatus allowed higher molecular weight polymers to be produced, but reaction times were lengthy. Even so, some monomer and solvent condensed in the gas trap, due to ineffective refluxing. Monomer and solvent were removed from the apparatus when the

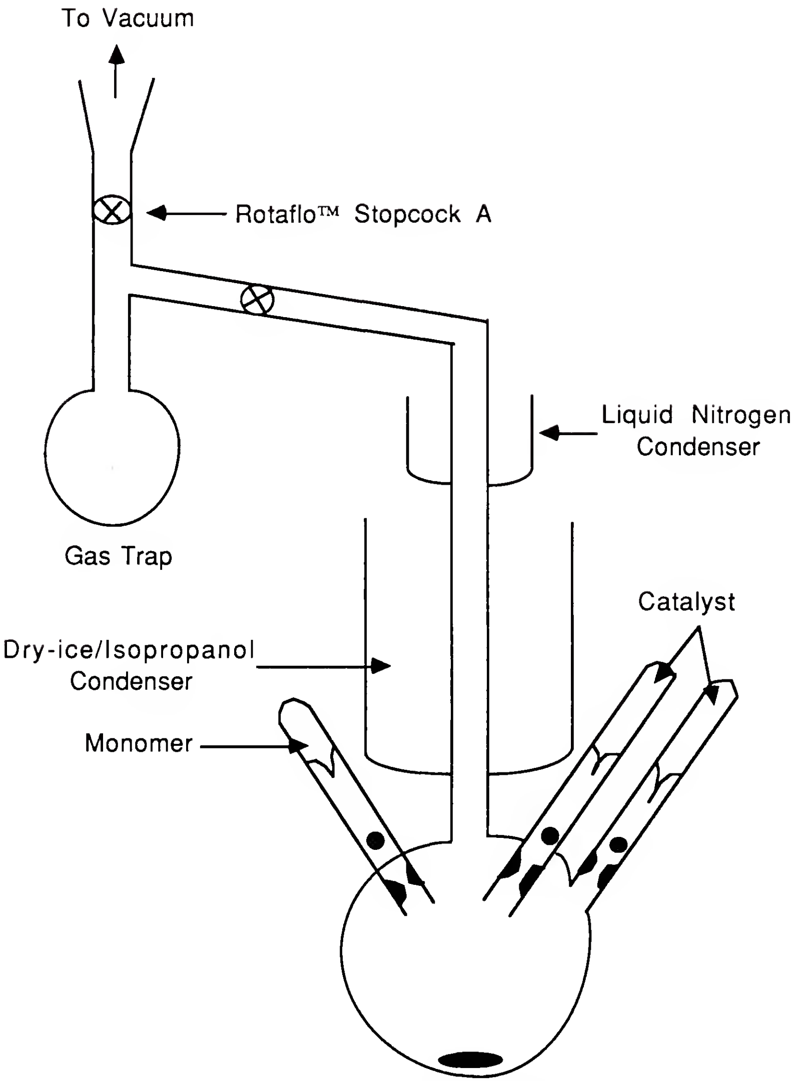


Figure 2-8. Acyclic diene metathesis polymerization apparatus

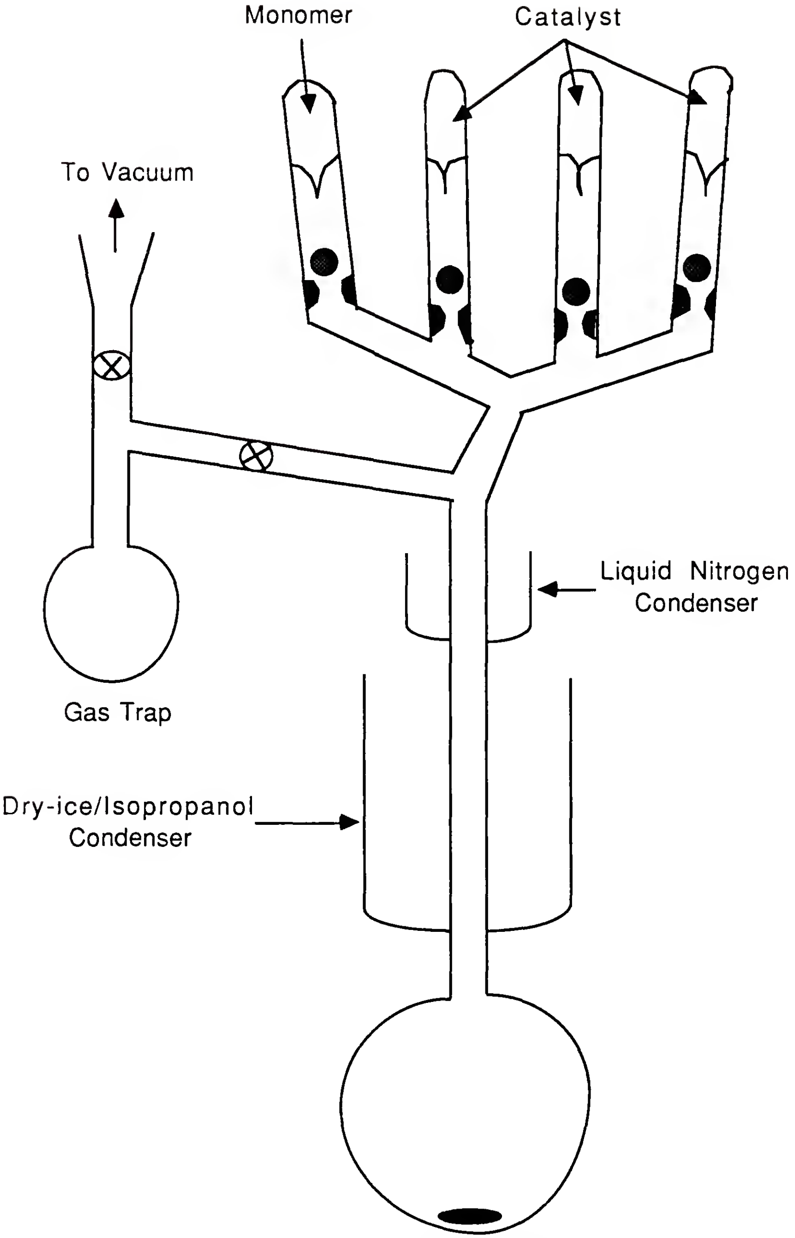


Figure 2-9. Acyclic diene metathesis polymerization apparatus with monomer and catalyst breakseals above reaction section.

ethylene was pumped out, resulting in lower yields, and the use of this apparatus was discontinued.

A major problem in conducting the polymerizations proved to be the premature precipitation of the product. In order to decrease reaction times by more effective refluxing of solvent and monomer, modifications were made to the apparatus (Figure 2-10). Modifications allowed for the controlled removal of ethylene without loss of monomer. The polymer could be heated continuously while kept in solution, thereby, remaining in contact with the catalyst.

All polymerizations were conducted by first transferring the catalyst solution from a breakseal ampule to the reaction vessel, then removing the solvent (pentane, in this case). A solid deposit of catalyst residue remained, and the monomer was introduced from its breakseal ampule directly into the reaction vessel containing this catalyst. Upon addition of the monomer, a gas was released instantly, which was determined to be pure ethylene by GC mass spectrometry. Ethylene was continuously removed from the vessel and solidified in a liquid nitrogen trap built into the reaction vessel. The monomer also distilled in the process, but was trapped with a partial condenser and returned to the reaction vessel.

All polymerizations either were performed using carefully dried toluene as the solvent, or under bulk conditions (no solvent at all). The temperature of the reaction was varied between 20-75°C. All polymerizations were terminated by exposure to the atmosphere.

The products were purified by dissolving in benzene and

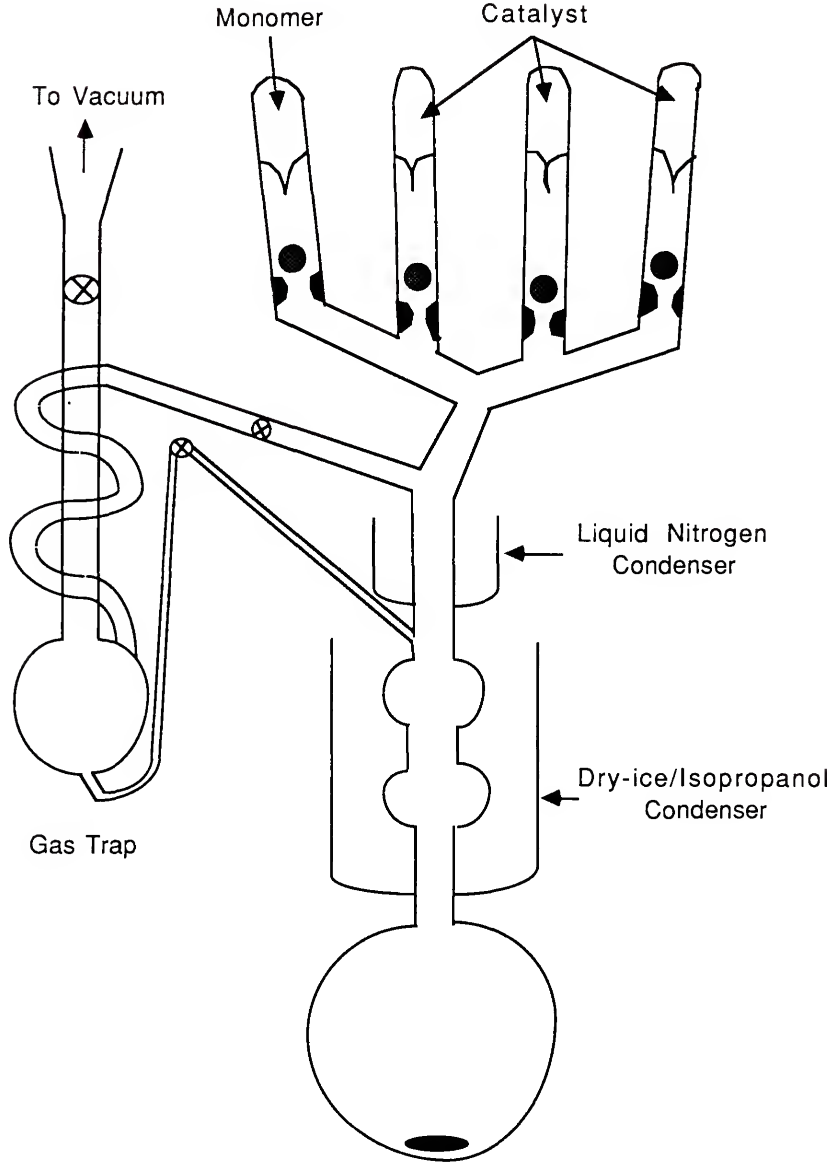


Figure 2-10. Acyclic diene metathesis polymerization apparatus with capillary return line, spiral gas trap and bubble condenser.

precipitation with methanol. White solids for the high molecular weight samples and soft elastomers for the oligomers were found.

Reaction Conditions for 1,9-Decadiene Polymerizations

To optimize the reaction conditions for the acyclic diene metathesis polymerization of 1,9-decadiene several different reactions were performed with the goal of obtaining high molecular weight polymer samples in the shortest possible reaction times. The effect of a large volume of solvent on the molecular weight of the resulting polymer was examined in this reaction.

Reaction 1. Approximately 2 ml of purified 1,9-decadiene and 40 ml of toluene were used. Four successive additions of catalyst 2, 8 hours apart, were made. The reaction temperature was kept at 25°C for a total reaction time of 32 hours. The reaction time was not optimal, since the experimental conditions were unknown and had to be refined. The results of the reaction were:

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 139.1 ppm (terminal vinyl methylene carbons),130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 114.1 ppm (terminal vinyl methine carbons), 32.7 and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

Molecular Weight ($\overline{Mn}$): 1700 (end-group analysis).

Reaction 2. In order to evaluate bulk polymerization conditions,1,9-decadiene (25 ml) and 3 additions of catalyst 2 were added 12 hours apart. The temperature was raised by 5°C increments in order to keep the polymer in the liquid state, up to 50°C. No solvent was used. The total reaction time was 40 hours. A long reaction time was used due to the ineffective refluxing of the monomer that prevented it from being in constant contact with catalyst. The following results revealed that polyoctenamer was produced:

^1H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 139.1 ppm (terminal vinyl methylene carbons),130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 114.1 ppm (terminal vinyl methine carbons), 32.7 and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

CHN: %C = 87.27, %H = 12.73 (Theory)

%C = 87.16, %H = 12.68 (Found)

Molecular Weight ($\overline{Mn}$): 11 000 (end-group analysis); 12 000 (VPO).

Viscosity [n]: 0.26 dL/g

Reaction 3. Approximately 2 ml of monomer was run under bulk conditions at 25°C for I 1/2 hours during which the polymer completely solidified. A large volume of toluene, approximately

100 ml, was vacuum transferred into the reaction vessel, and the reaction temperature was increased from 25°C to 50°C. Two more additions of catalyst 2 were made fifteen hours apart, and the reaction was exposed to continuous vacuum for 40 hours. In order to compare Reaction 3 with previous reactions, a long reaction time was employed. Oligomeric polyoctenamer was produced as indicated by the following results:

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 139.1 ppm (terminal vinyl methylene carbons), 130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 114.1 ppm (terminal vinyl methine carbons), 32.7 and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

Molecular Weight ($\overline{Mn}$): 1600 (end-group analysis).

Reaction 4. The minimum amount of solvent that would facilitate magnetic agitation, and its effect on the reaction was tested. Approximately 2 ml of monomer was used and 3 additions of catalyst 2 were made; one at the start of the reaction and the rest as described below. The temperature was slowly raised to 50°C and when the polymer solidified, 10 ml of toluene were added together with another aliquot of catalyst at 25°C. The reaction temperature was raised slowly to 50°C over a period of six hours. A third addition of catalyst 2 was made after which the reaction allowed to continue for an additional 24 hours. The following results were obtained:

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 32.7 and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

CHN: %C = 87.27, %H = 12.73 (Theory)
%C = 87.11, %H = 12.68 (Found)

Molecular Weight ($\overline{Mn}$): 57 000 (SEC); ($\overline{Mw}$): 108 000 (SEC)
Viscosity [n]: 0.89 dL/g

Reaction 5. The effect of increased reaction temperature on the activity of the catalyst was investigated. Approximately 2 ml of monomer was polymerized using a double addition of catalyst 2. The second addition of catalyst 2 was made after one week, and no solvent was used throughout the reaction. A temperature of approximately 75°C was maintained while a high vacuum was applied for 2 weeks. Results of the benzene soluble portion were:

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 139.1 ppm (terminal vinyl methylene carbons),130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 114.1 ppm (terminal vinyl methine carbons), 32.7

and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

Molecular Weight ($\overline{Mn}$): 3000 (end-group analysis).

Reaction 6. The possible formation of cyclic compounds at short reaction times was investigated. Monomer (0.5 ml of 1,9-decadiene) was added to 20 mg of catalyst 2 after removal of pentane from the catalyst, and bulk polymerization conditions were employed. The reaction temperature was kept at 25°C and after 20 minutes the monomer had polymerized sufficiently to solidify, after which the reaction was terminated by exposure to the atmosphere. The obtained results were:

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 139.1 ppm (terminal vinyl methylene carbons), 130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 114.1 ppm (terminal vinyl methine carbons), 32.7 and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

Molecular Weight ($\overline{Mn}$): 2500 (end-group analysis).

Reaction 7. Bulk reaction conditions over a shortened reaction time were investigated. A bulk polymerization was carried out on 1 ml of 1,9-decadiene, using a single addition of catalyst 2. The polymer solidified after 30 minutes and the temperature was raised to between 50 and 55°C. A high vacuum was applied for 10 hours after which the reaction was terminated. The following results were obtained:

^1H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 32.7 and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

CHN: %C = 87.27, %H = 12.73 (Theory)
%C = 87.18, %H = 12.69 (Found)

Molecular Weight ($\overline{Mn}$): 25 000 (VPO).

Viscosity [n]: 0.39 dL/g

Reaction 8. The possibility of further polymerizing an existing polymer was investigated. A portion of the polyoctenamer sample (1 g) formed in reaction 2 was dissolved in 20 ml of toluene, syringed into the reaction vessel and then subjected to four freeze-thaw-vacuum cycles. A single addition of catalyst 2 was made, and the reaction temperature was slowly raised to 65°C. The reaction was allowed to proceed for 36 hours after which it was terminated by exposure to the atmosphere, obtaining the following results:

^1H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.35 ppm (internal olefinic protons), 1.95 and 1.25 ppm (methylene protons).

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 130.4 and 129.8 ppm (trans and cis internal olefinic carbons), 32.7 and 27.3 ppm (trans and cis methylene carbons adjacent to internal olefinic carbons), 29.8 and 29.1 ppm (methylene carbons).

CHN: %C = 87.27, %H = 12.73 (Theory)

%C = 87.20, %H = 12.71 (Found)

Molecular Weight ($\overline{Mv}$): 83 000 (viscosity).

Viscosity [n]: 0.76 dL/g

The Acyclic Diene Metathesis (ADMET) Polymerization of 1,5-Hexadiene.

General polymerization Procedure.

The metathesis of 1,5-hexadiene to linear poly-1,4-butadiene was investigated, using a Lewis acid free catalyst. The monomer, 1,5-hexadiene, was purified in the same manner as for 1,9-decadiene. The catalyst solution and apparatus were unchanged from that used in producing polyoctenamer (ie., 20 mg of catalyst 2, $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$, and the apparatus shown in Figure 2-10).

Reaction Conditions for 1,5-Hexadiene polymerizations

Two polymerizations were conducted. In the first polymerization, 50 ml toluene (2.53×10^{-5} mol) were used as the solvent. Three additions of catalyst, 20 mg per addition, were made to approximately 5 ml (6.0×10^{-2} mol) of 1,5-hexadiene. The three additions of catalyst were made approximately 24 hours apart. The reaction temperature was kept at 25°C, while the reaction was continuously stirred for a period of two months. Since the reaction had been reported to be impossible [56], an excessively long reaction time was used in the first reaction. The lifetime of the catalyst is also unknown and an extensive reaction time was used to give some indication of the activity of the catalyst over a long period of time. A slight vacuum was occasionally applied to remove the ethylene produced.

The product was purified by dissolving in benzene and precipitating the polymer with methanol. The resulting elastomeric polymer, obtained in a quantitative yield, was light yellow in color. The following results were obtained:

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.42 ppm (internal olefinic protons) and 2.05 ppm (methylene protons)

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 130.0 and 129.4 ppm (trans and cis internal olefinic carbons) and 32.7 and 27.5 ppm (trans and cis methylene carbons)

CHN: %C = 88.82, %H = 11.18 (Theory)
%C = 88.61, %H = 11.16 (Found)

Molecular Weight ($\overline{Mn}$): 8300 (SEC); ($\overline{Mw}$): 16 400 (SEC)

The second reaction was done in order to compare the ability of the catalyst to polymerize 1,5-hexadiene under bulk reaction conditions. The reaction was modeled after reaction 7 of the 1,9-decadiene series, where bulk reaction conditions were employed. A single aliquot (20 mg.; 2.5 x 10^{-5} mol) of catalyst and 2 ml (0.024 mol) of 1,5-hexadiene was used. The reaction temperature was maintained at 25°C until the polymer could no longer be stirred by magnetic agitation. The reaction temperature was then increased to 52°C and a continuous high vacuum (10^{-6} mmHg) applied. The polymer's viscosity increased over the next 5 hours, after which it could no longer be agitated and the reaction was terminated. The total reaction time of the second reaction was 10 hours.

The product was purified by dissolving it in benzene and precipitating with methanol. The resulting elastomeric polymer, obtained in near quantitative yields, was light yellow in color. The following results were obtained:

^{1}H NMR ($CDCl_3$, 200 MHz, δ in PPM): 5.42 ppm (internal olefinic protons) and 2.05 ppm (methylene protons)

^{13}C NMR ($CDCl_3$, 50 MHz, δ in PPM): 130.0 and 129.4 ppm (trans and cis internal olefinic carbons) and 32.7 and 27.5 ppm (trans and cis methylene carbons)

CHN: %C = 88.82, %H = 11.18 (Theory)
%C = 88.54, %H = 11.22 (Found)

Molecular Weight ($\overline{Mn}$): 14 000 (SEC); ($\overline{Mw}$): 28 000 (SEC)

CHAPTER 3
THE KEY TO SUCCESSFUL ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION CHEMISTRY.

Competing side reactions are one of the major factors that determine if a given reaction is suitable for equilibrium step propagation, condensation type polymerization. Even a very small percentage of side reactions will prevent the principal reaction from producing high molecular weight polymer, leading instead to the formation of low molecular weight oligomers, and perhaps other undesirable by-products.

Previous polymerization studies on acyclic dienes revealed that more than olefin metathesis polymerization was taking place [58]. While metathesis chemistry appears to be the dominant reaction, vinyl addition chemistry does compete with acyclic olefin metathesis. Thus, vinyl addition reactions must be eliminated completely in order for acyclic diene metathesis polymerization to be useful chemistry.

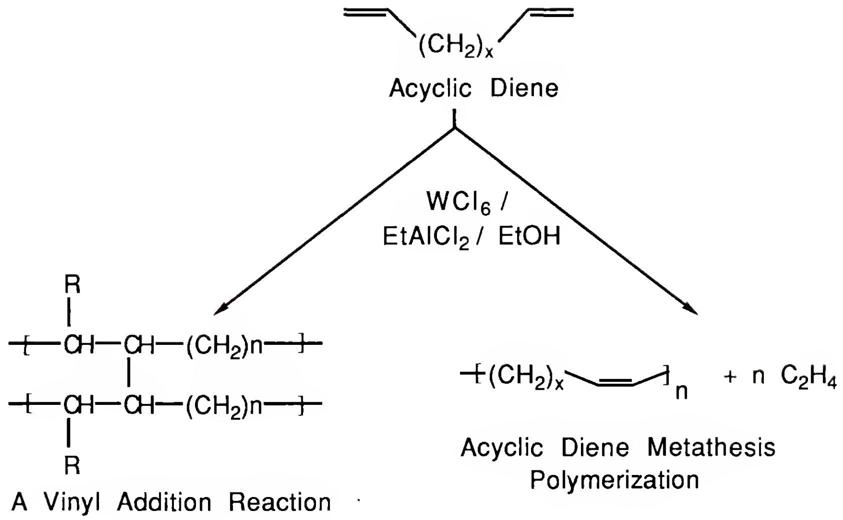


Figure 3-1. The possible reactions that can occur when a Lewis acid is used as cocatalyst.

Styrene as a Model Compound

A model compound study was undertaken to investigate the elimination of side reactions. Vinyl addition chemistry was expected to be the principal side reaction that was occurring, and a model compound system that would allow a simultaneous investigation of vinyl addition and metathesis chemistry was selected. The reaction of styrene was chosen, since benzyl carbocations can be formed quite easily, which would permit the vinyl addition reaction to compete directly with metathesis. In order to study the competition between metathesis and vinyl addition chemistry (Figure 3-1), bulk reactions of styrene were examined with $WCl_6/EtAlCl_2$ as the catalyst. The styrene reaction is an excellent model system, since vinyl addition would lead to polystyrene [64], whereas metathesis would lead to stilbene. Both styrene and stilbene can be readily identified by spectroscopic methods [65] even when a mixture of products is produced. In fact, vinyl addition chemistry proved to be the only reaction occurring, presumably because of the cationic polymerization of styrene (Figure 3-2) with no stilbene being observed.

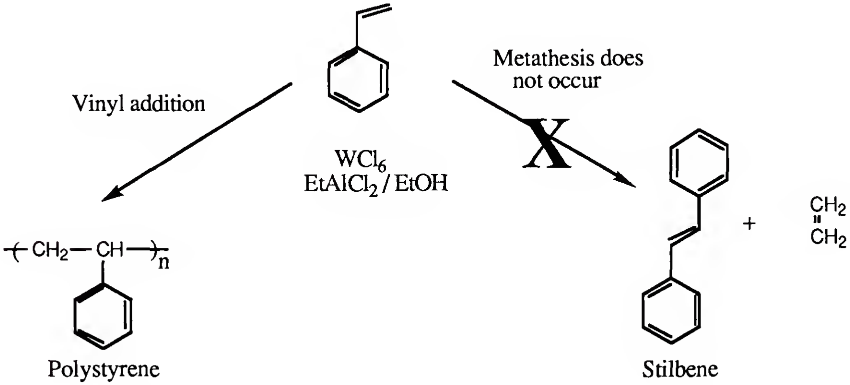


Figure 3-2. Attempted metathesis of styrene using a Lewis acid catalyst system.

The main competing side reaction is believed to be the cationic polymerization of styrene. Cationic polymerization can be initiated by the Lewis acid used as cocatalyst in the classical reaction scheme (Figure 3-2), and consequently, model reactions were conducted to eliminate these vinyl addition reactions.

The minimization of vinyl addition reaction (polymerization) was investigated by varying the sequence of addition of reactants into the reaction vessel (Table 3-1).

Table 3-1. Order of addition of reactants in the styrene model reaction.

First	Second	Last
Catalyst	Co-catalyst	Styrene
Catalyst	Reagent	Cocatalyst
Cocatalyst	Reagent	Catalyst
Cocatalyst	Catalyst	Reagent
Reagent	Catalyst	Cocatalyst
Reagent	Cocatalyst	Catalyst

The catalyst and cocatalyst were allowed to react for varying amounts of time at various temperatures prior to the addition of reagent. No change in the products was observed, and only polystyrene was identified as the product of the reaction.

The cocatalyst solvent, hexane, was removed either immediately after the catalyst and cocatalyst were combined, or after the catalyst and cocatalyst were allowed to react for some time. No change in the chemistry was observed.

Three solvents were examined, including chlorobenzene, which is the most widely used solvent with this specific catalyst system [66]. Because cationic polymerization of styrene occurs instead of metathesis, solvents of lower dielectric constants were used. Solvents of low dielectric constant are known to eliminate the formation of ions [67], thus possibly preventing cationic polymerization. Carbon tetrachloride (2.0) and hexane (5.7) were tried, but no change in the chemistry was observed.

When Schlenk vacuum line techniques were used, the analysis of the gases produced frequently indicated the presence of ethane. Evidently, trace amounts of moisture were present that reacted with the $EtAlCl_2$ to produce ethane. In order to assure absolute purity and dryness of the reagents, and the apparatus, high vacuum techniques were employed. Under these conditions no ethylene was observed in the styrene reactions, indicating that metathesis did not occur, and only cationic polymerization was observed.

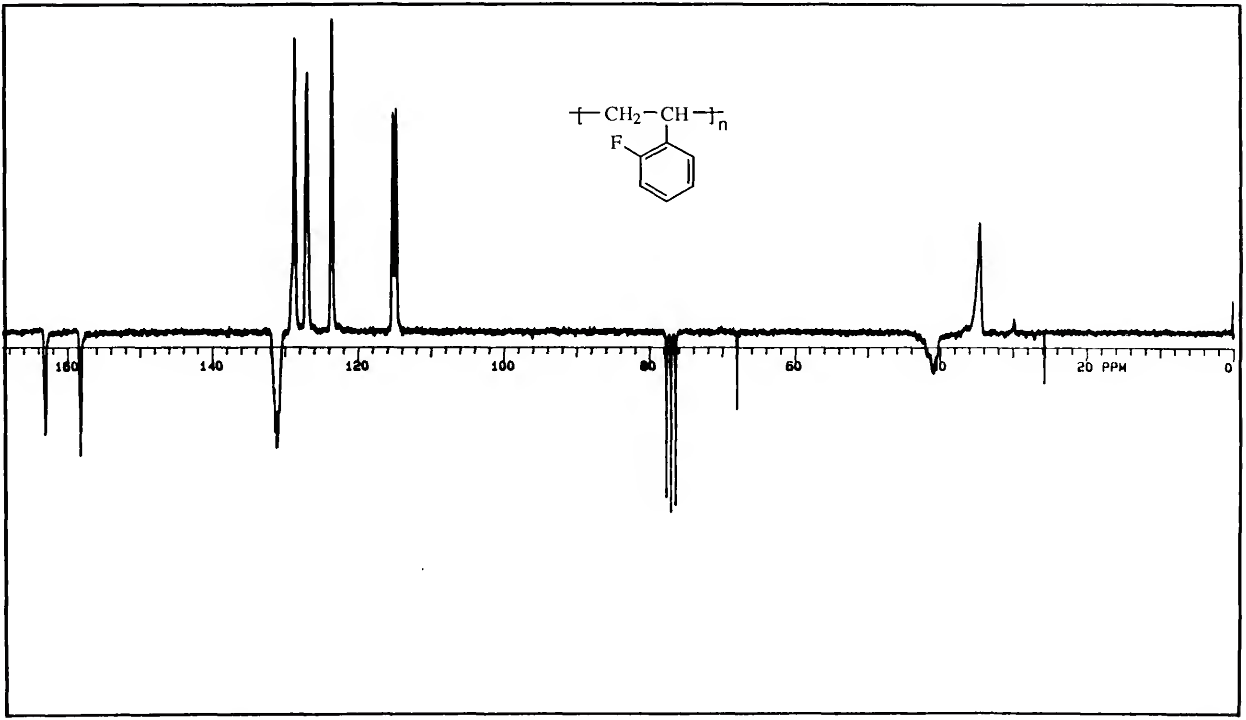
Since the Lewis acid ($EtAlCl_2$) initiated vinyl addition, different cocatalysts (Et_2AlCl and Et_3Al) were tried. No stilbene was produced, and as before, only polystyrene resulted.

The use of different reaction conditions, addition sequences, solvents, and Lewis acid cocatalysts proved to be unsuccessful, and it can be concluded that the metathesis of styrene does not occur when WCl_6 and an alkyl-aluminum containing Lewis acid is used as the catalyst system.

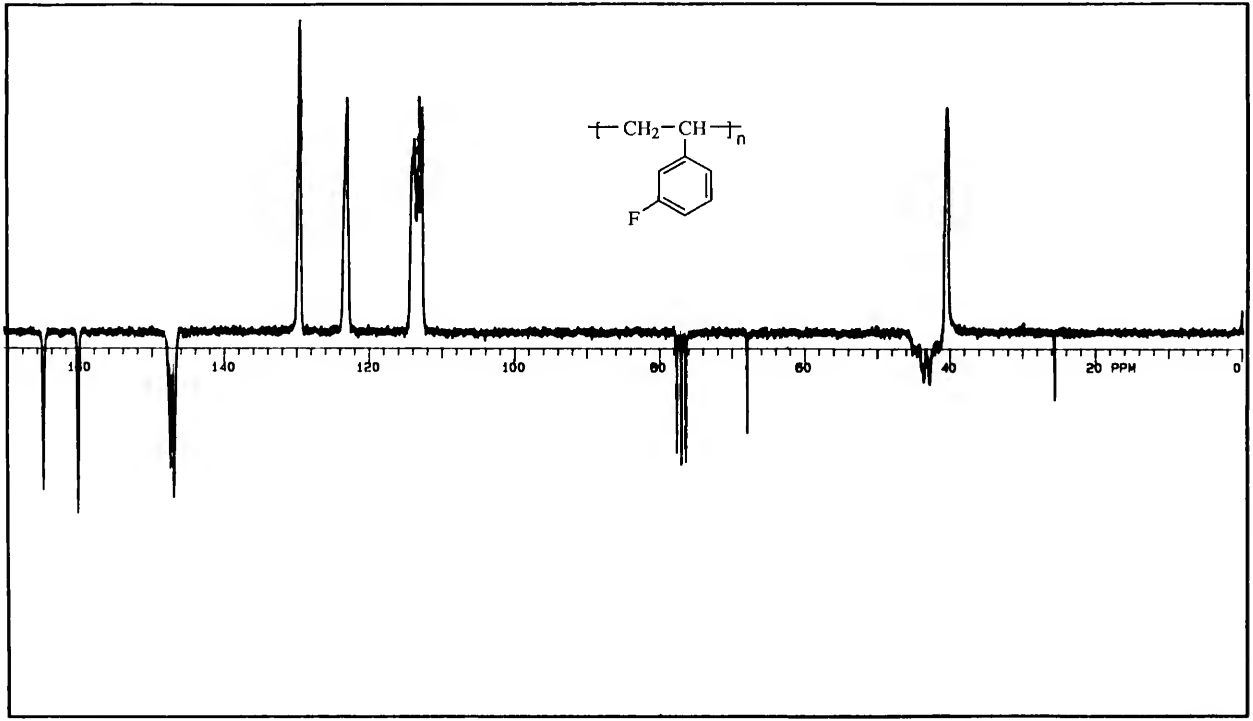
Preventing the Cationic Polymerization of Styrene

In an effort to destabilize styrene toward cationic polymerization, four fluorinated styrenes (2-fluorostyrene, 3-fluorostyrene, 4-fluorostyrene and 2,3,4,5,6-pentafluorostyrene) were investigated with the $WCl_6/ETAlCL_2$ catalyst system. By reducing the electron density in the vinyl bond of styrene the likelihood of forming styrene carbocations might be eliminated, thereby reducing styrene's propensity to undergo vinyl addition polymerizations. In each case, however, vinyl addition predominated. Although the reaction proceeded at a slower rate, the only products observed were fluorinated polystyrenes. A comparison of the NMR spectra of the products formed with NMR spectra of authentic fluorinated polystyrenes (Spectra 3-1, 3-2), prepared by anionic polymerization, indicates that only fluorinated polystyrenes were produced. 2,3,4,5,6-Pentafluorostyrene polymerized the slowest of all the fluorinated styrenes that were used, and when high vacuum techniques were employed, 2,3,4,5,6-pentafluorostyrene did not react at all, indicating that destabilization of the carbocation does indeed prevent carbocation formation.

In order to test for catalyst activity in the fluorinated systems, an acyclic diene known to undergo metathesis oligomerization (i.e., 1,9-decadiene), was added to the reaction after 24 hours, which metathesized to give polyoctenamer of low molecular weight and some intractable material [58]. A metathesis active catalyst system obviously was present, and apparently, the electron withdrawing nature and the bulkiness of the fluorine groups on the 2,3,4,5,6-pentafluorostyrene prevent this reagent from either polymerizing or metathesizing



Spectrum 3-1. 50 MHz ^{13}C NMR of poly-2-fluorostyrene formed by anionic polymerization techniques.



Spectrum 3-2. 50 MHz ^{13}C NMR of poly-3-fluorostyrene formed by anionic polymerization techniques.

Investigation of a Lewis Acid Free Catalyst System with Styrene as the Model Compound

The use of Lewis acid free catalysts could obviate the formation of carbocations, thereby eliminating vinyl addition reactions. Efforts were focused on choosing an appropriate catalyst system which would be less acidic and would not induce vinyl addition polymerization. The homogeneous metathesis catalyst prepared by Schrock [62, 63] was chosen because it is free of Lewis acids. Schrock reported that the catalyst was extremely active for the metathesis of internal olefins, yet, under the reaction conditions reported, styrene, 1-octene, and allyltrimethylsilane metathesized slowly [62].

While these results were encouraging, it was not apparent if these catalysts would be suitable for acyclic diene metathesis polymerization. Two derivatives of the catalyst, types 1 and 2 (Figure 2-2, page 22), were chosen since they are reported to be the least active (catalyst 1) and most (catalyst 2) active metathesis catalysts for internal olefins. Catalyst 1 produced stilbene from styrene. However, under similar reaction conditions, the reaction rates were much slower compared to catalyst 2. Preliminary styrene metathesis results and the metathesis of cis-2-pentene [63] led to the exclusive use of catalyst 2 in subsequent studies.

Reaction conditions were chosen that were appropriate for modeling bulk polymerization reactions. Specifically, no solvent was used as is appropriate for equilibrium step propagation, condensation polymerization chemistry [68], and when using catalyst 2 (page 22), the mechanism for the styrene reaction changed completely from vinyl addition to metathesis chemistry (Figure 3-3).

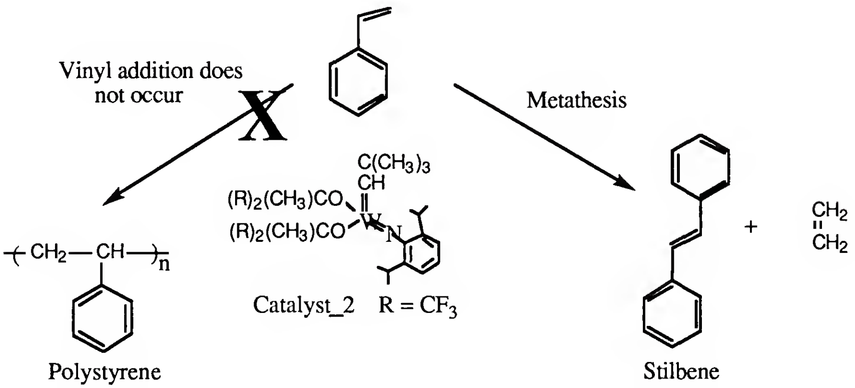
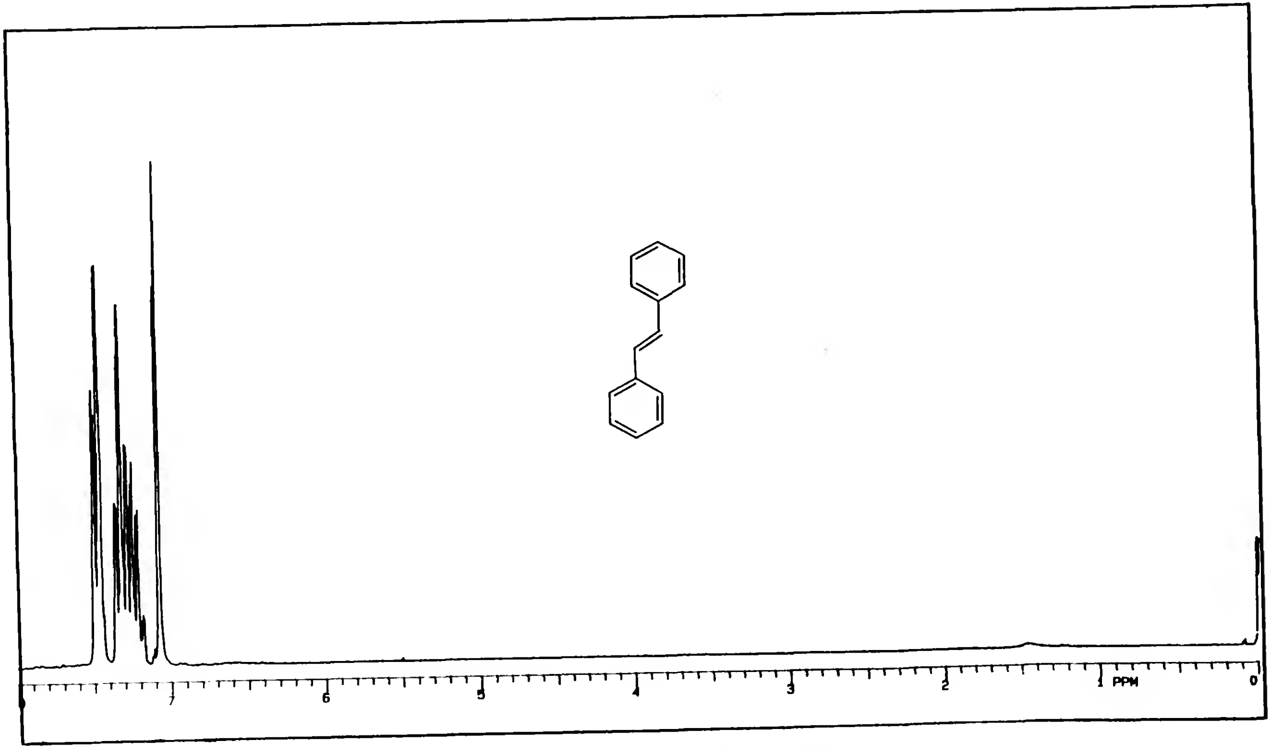


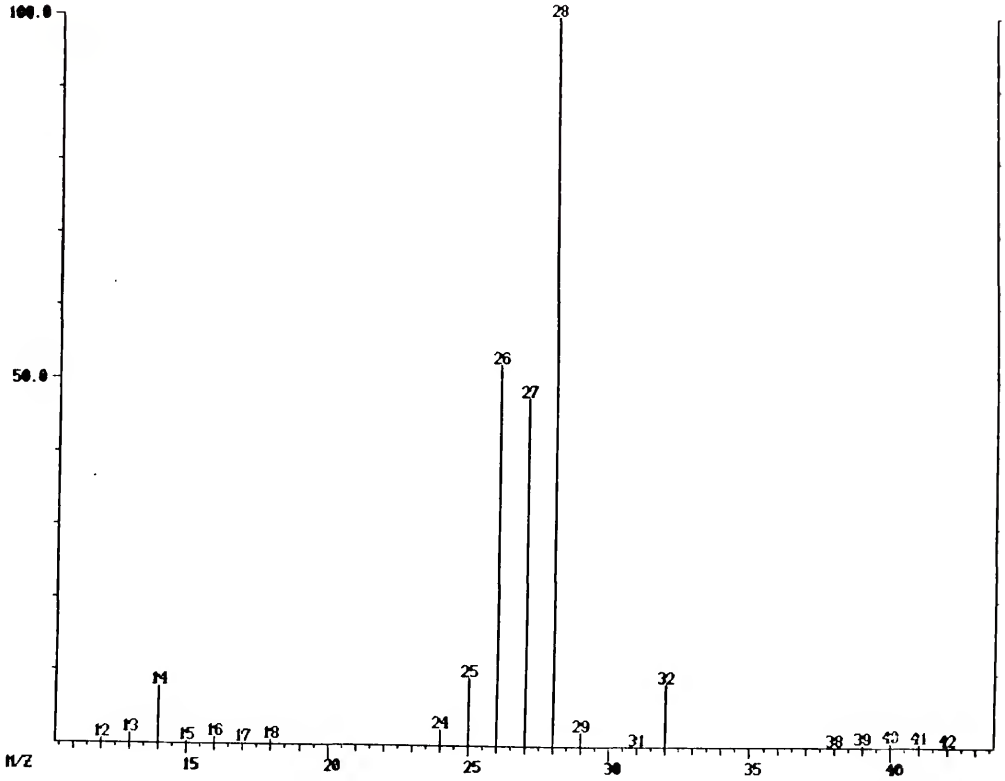
Figure 3-3. Styrene metathesis using a Lewis acid free catalyst.

Metathesis occurs quantitatively, a result which represents a spectacular change from the previous result shown in Figure 3-2. The reaction was permitted to continue over a two hour period, and no side reactions (i.e., vinyl addition reactions) were observed. The NMR spectrum 3-3 of the unpurified product only shows resonances that are indicative of trans stilbene. No other products were present.

The gas formed during the reaction was analyzed by mass spectroscopy (Spectrum 3-4), which shows that only ethylene was produced by the reaction (expected if only metathesis occurred).



Spectrum 3-3. 200 MHz ^{1}H NMR of unpurified trans stilbene produced by the metathesis of styrene with a Lewis acid free catalyst.

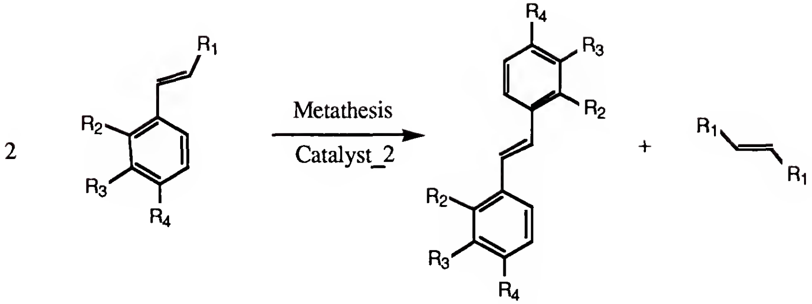


Spectrum 3-4. Mass Spectrum showing parent ion peaks of ethylene released when metathesis reactions and polymerizations are performed using a Lewis acid free catalyst.

Investigation of a Lewis Acid Free Catalyst System with Substituted Styrenes as Model Compounds

In order to demonstrate the potential of this olefin metathesis reaction, a variety of substituted styrenes were investigated, and the reactions in Figure 3-4 indicate the versatility of the Lewis acid free catalyzed metathesis reaction. Using a Lewis acid free catalyst system, 2-fluorostyrene (Reaction A), 3-fluorostyrene (Reaction B) and 4-fluorostyrene (Reaction C) all metathesize cleanly and produce the analogous substituted stilbenes in a manner much the same as for styrene.

The reactions were carried out over a 24 hour period in the reaction vessel (Figure 2-5) designed for styrene reactions. Powderous, substituted stilbenes in essentially quantitative yields were obtained. Reaction times were not optimal, nor were they indicative of the rate of the reactions, and it is expected that under optimal reaction conditions, reaction times will be considerably shortened. The products were pure as is shown by the NMR spectra 3-5, 3-6 and 3-7. Elemental analysis substantiated the exclusive formation of substituted stilbenes without a trace of any vinyl addition products.



Reaction A $R_1 = R_3 = R_4 = H$; $R_2 = F$

Reaction B $R_1 = R_2 = R_4 = H$; $R_3 = F$

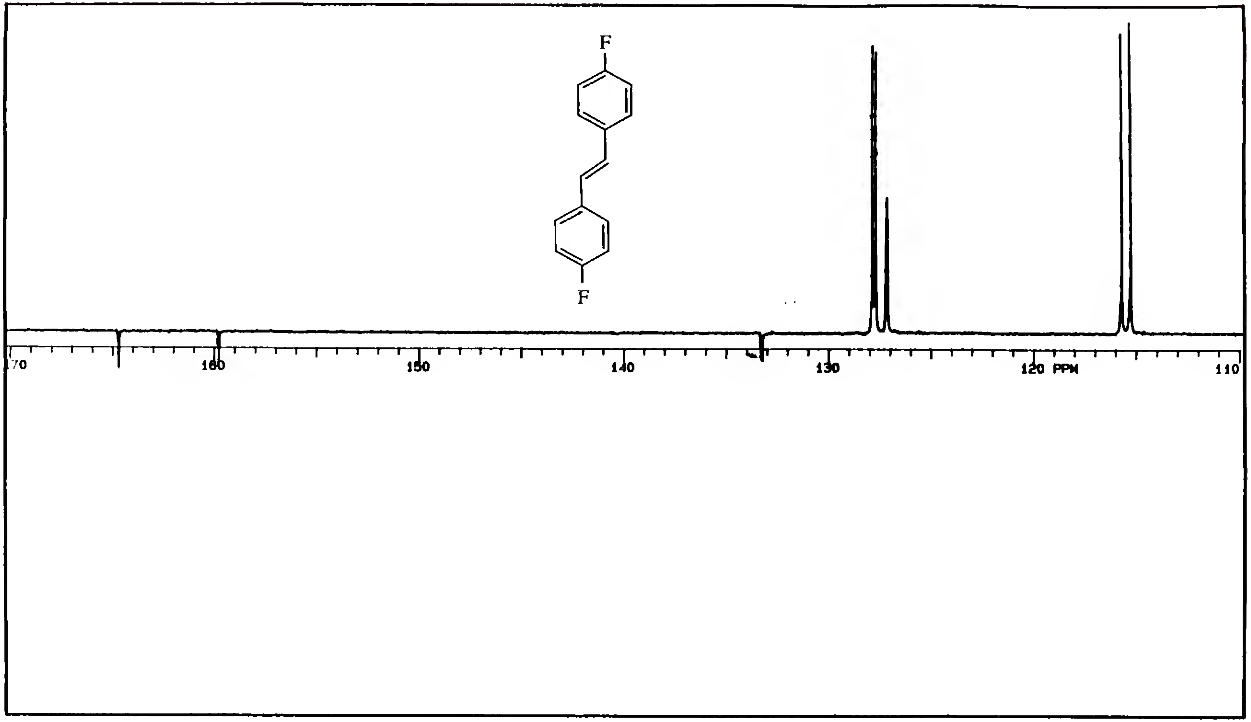
Reaction C $R_1 = R_2 = R_3 = H$; $R_4 = F$

Reaction D $R_1 = R_2 = R_4 = H$; $R_3 = Br$

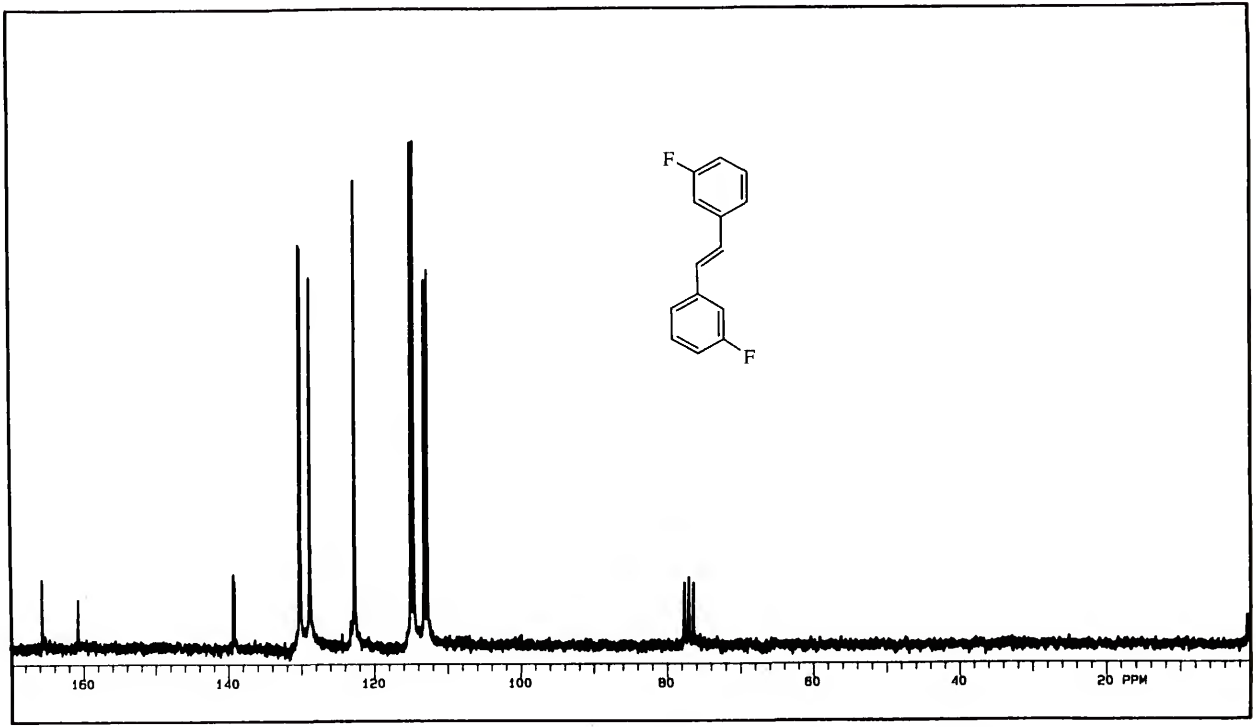
Reaction E $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$

Figure 3-4. The Metathesis of substituted styrenes.

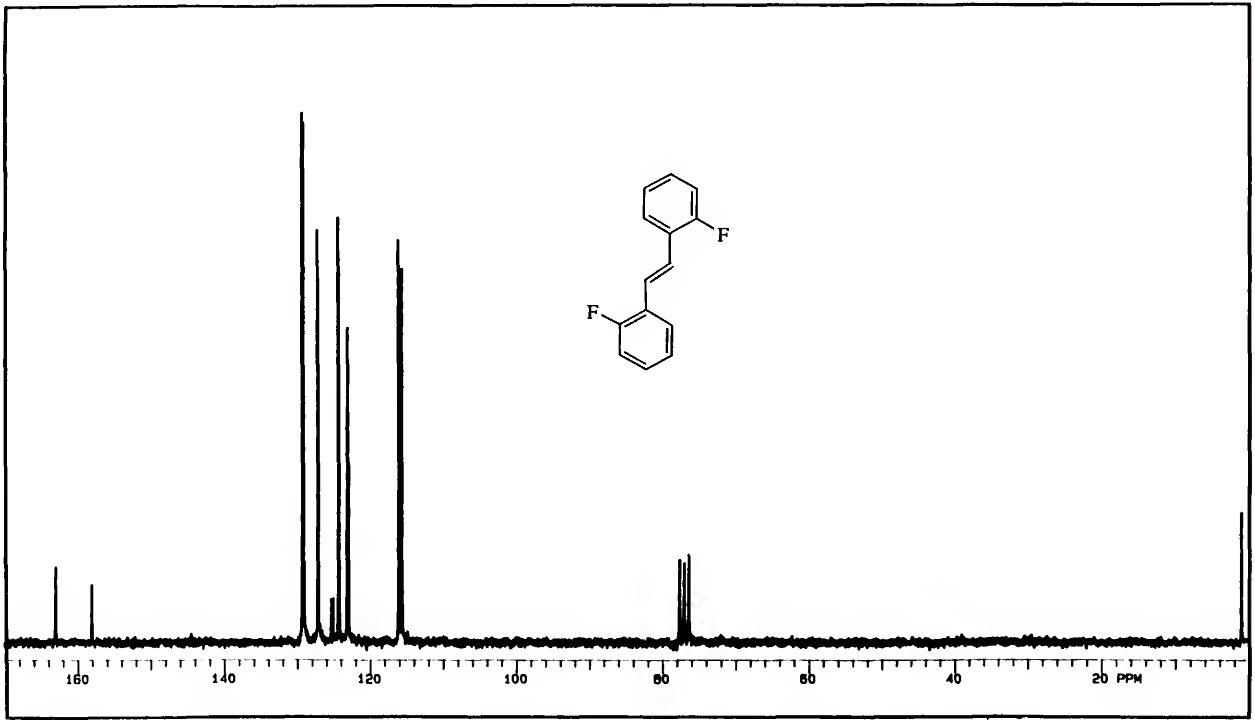
Producing substituted stilbenes in high yields and purity is in sharp contrast to the previous methods used to prepare these products [69 70, 71 72]. The preparation of 4,4-difluorostilbene by Ager [73] in 1972, using the synthetic route shown in Figure 3-5, is a prime example of the lengthy, low yield reactions previously used



Spectrum 3-5. 50 MHz ^{13}C NMR of 4,4'-difluorostilbene produced by the metathesis of 4-fluorostyrene with a Lewis acid free catalyst.

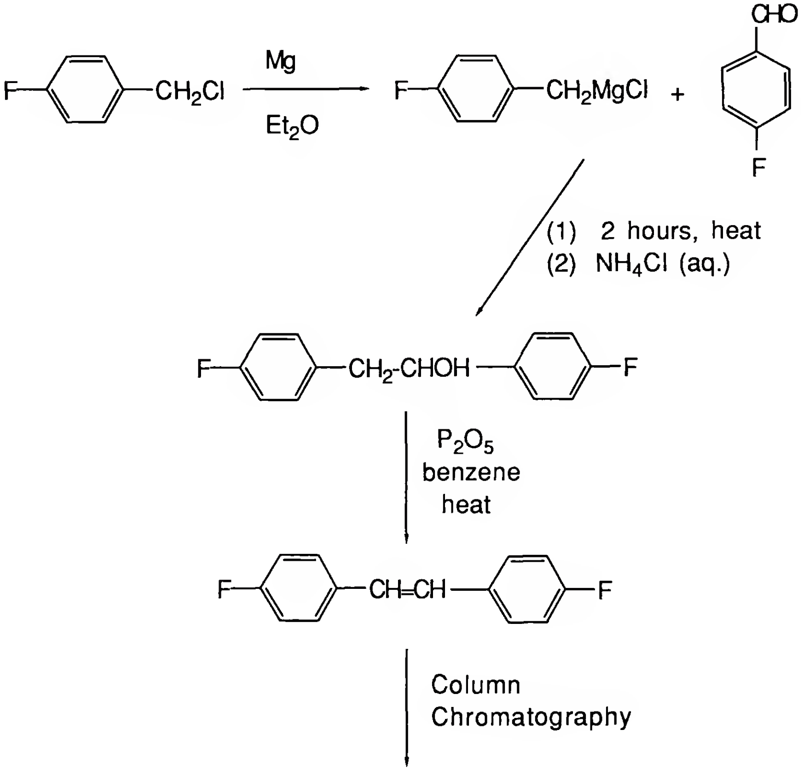


Spectrum 3-6. 50 MHz ^{13}C NMR of 3,3'-difluorostilbene produced by the metathesis of 3-fluorostyrene with a Lewis acid free catalyst.



Spectrum 3-7. 50 MHz ^{13}C NMR of 2,2'-difluorostilbene produced by the metathesis of 2-fluorostyrene with a Lewis acid free catalyst.

in the synthesis of substituted stilbene compounds. Obviously, metathesis provides a much more efficient, single step synthetic method. Yields of previous synthetic methods ranged from 10-30 %, and mixtures of products were always observed which made purification difficult.



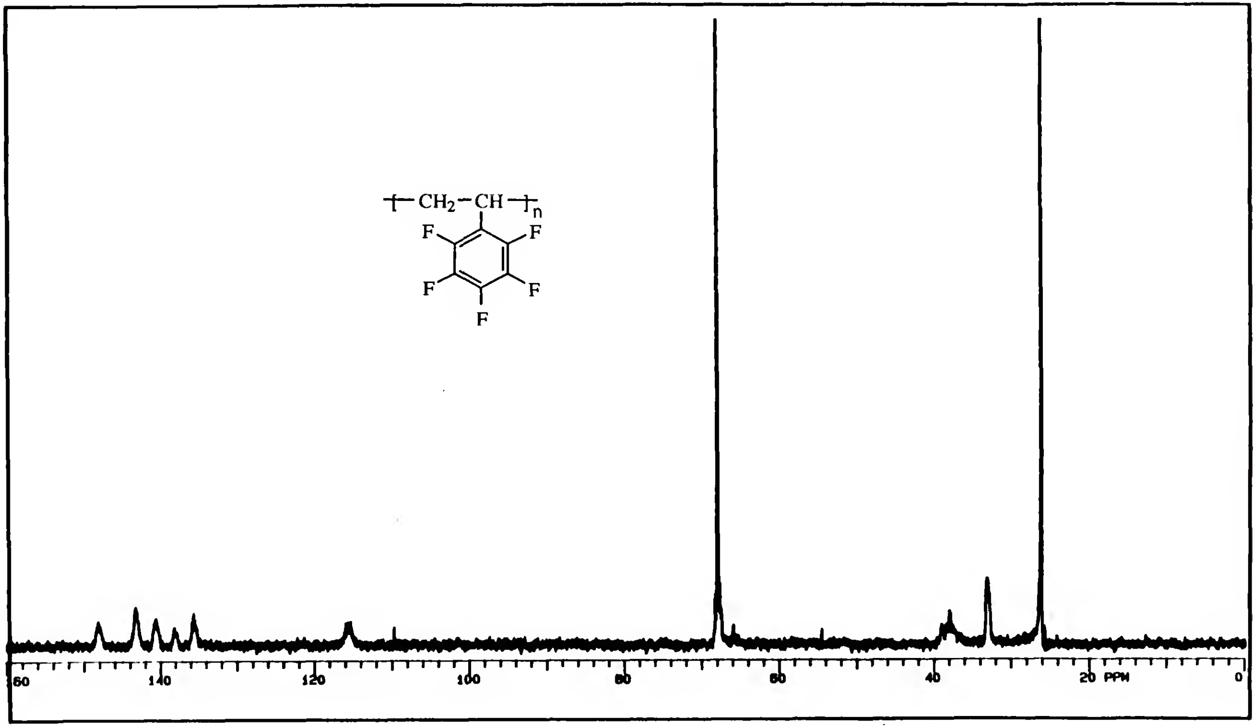
trans 4,4'-difluorostilbene (10% yield)

Figure 3-5. Synthesis of 4,4'-difluorostilbene

2,3,4,5,6-Pentafluorostyrene did not react at all under these reaction conditions. If the reaction is heated to 70°C, poly-2,3,4,5,6-pentafluorostyrene is formed (Spectrum 3-8). A second addition of catalyst also proved to be ineffective. No decafluorostilbene was produced. Two possible reasons why 2,3,4,5,6-pentafluorostyrene does not metathesize are:

(1) The five fluorine atoms have such a strong electron withdrawing effect on the molecule that the electron density of the vinyl bond is diminished to the extent that it cannot coordinate with the already electron deficient catalyst metal center. The tungsten carbon double bond in the analogous benzylidene metal complex was found to be shorter when fluorinated alkoxide ligands were present than in the presence of non-fluorinated ligands [63]. Shortening of the tungsten carbon double bond was attributed to the electron withdrawing nature of the hexa-fluoro alkoxide ligand. A combination of the electron withdrawing effect of the hexafluoro alkoxide ligands and the diminished electron density of the pentafluorostyrene vinyl bond provide a plausible explanation for the unreactivity of 2,3,4,5,6-pentafluorostyrene.

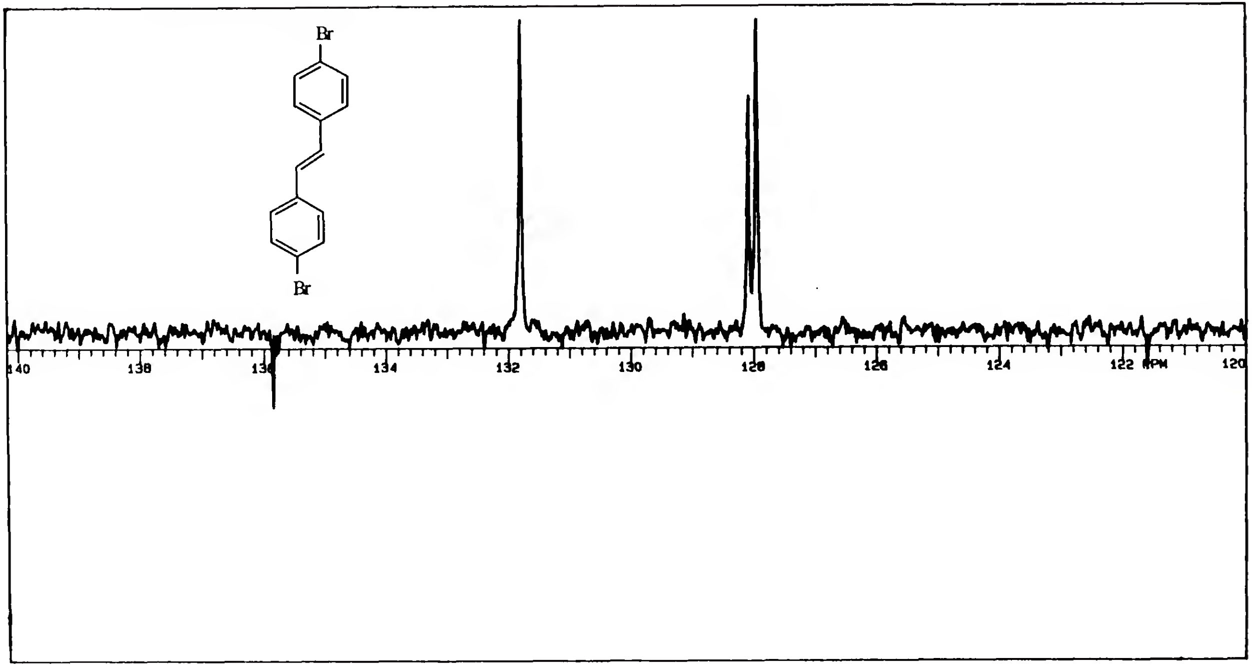
(2) Fluorine atoms are relatively small. Due to a high electron density, repulsion are experienced over long ranges, thus making fluorine bulky in terms of stereochemistry [63]. This "bulkiness" could be a factor in preventing the vinyl bond of 2,3,4,5,6-pentafluorostyrene from coming into close proximity with the catalyst to produce the metallocyclobutane ring intermediate, essential for metathesis to occur [25, 26, 27]. X-ray structural analysis of $W(CHPh)(NAr)[OCMe(CF_3)_2]_2$ indicates that the two



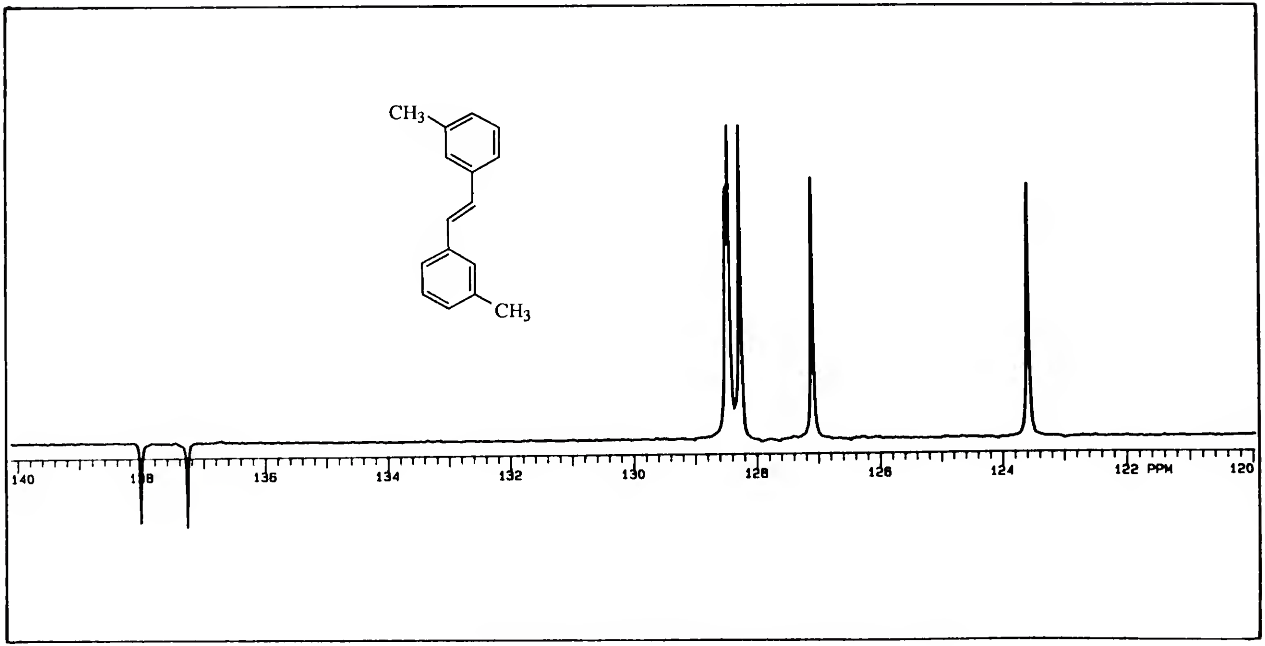
Spectrum 3-8. 50 MHz ^{13}C NMR of poly-penta-fluorostyrene formed due to the decomposition of the Lewis acid free metathesis catalyst at 75 °C.

alkoxide ligands are turned away from each other and also that the two tryfluoromethyl groups, in each alkoxide, are turned away from the benzylidene and imido ligands [62]. The presence of fluorine atoms at the two ortho positions of 2,3,4,5,6-pentafluorostyrene result in bigger steric repulsion between the alkoxide ligands and the pentafluoro benzylidene ligand. Van der Waals interactions between trifluoromethyl and hydrocarbon groups, as well as any interaction between triflouromethyl and the ortho fluorines on the pentaflourobenzylidene ligand must be diminished for a metallocyclobutane ring to be formed. Stereochemical overcrowding at the metal center may prevent a second 2,3,4,5,6-pentafluorostyrene molecule from approaching, thereby preventing the formation of a metallocyclobutane intermediate and subsequently metathesis.

4-Bromostyrene (Reaction D; Figure 3-4, page 69) and 3-methylstyrene (Reaction E Figure 3-4, page 69) metathesize cleanly and form the respective substituted stilbenes in quantitative yields, as confirmed by elemental analysis and NMR spectroscopy (Spectra 3-9,10). Cadogan and Inward [74] investigated the three possible methods [75, 76, 77] for the preparation of trans-4,4'-dibromostilbene and found that a modified version of the Bance, Barber and Woolman method [77], was the most satisfactory with yields slightly higher than 40%. The other two methods gave stilbene yields ranging from 3%-40%. All three methods involved multistep reactions and rigorous purification of the starting materials. It is evident that the single step metathesis reaction



Spectrum 3-9. 50 MHz ^{13}C NMR of 4,4'-dibromostilbene produced by the metathesis of 4-bromostyrene with a Lewis acid free catalyst.



Spectrum 3-10. 50 MHz ^{13}C NMR of 3,3'-dimethylstilbene produced by the metathesis of 3-methylstyrene with a Lewis acid free catalyst.

procedure with its essentially quantitative yield is the preferred route to produce stilbenes..

These model reactions demonstrate the versatility of the metathesis reaction system, and show that vinyl addition side reactions can been eliminated completely. The essentially quantitative yields fulfill the prerequisite of high percentage conversion (>99%) of monomer to polymer, required by step condensation type polymerization.

Expanding small molecule metathesis chemistry into a polymerization reaction is the next challenge. Acyclic diene metathesis polymerization would be the first new equilibrium step propagation condensation type polymerization in 20 years. Subsequent chapters elaborate on the feasibility and implementation of the acyclic diene metathesis polymerization technique.

CHAPTER 4

ACYCLIC DIENE METATHESIS POLYMERIZATION (ADMET). THE SYNTHESIS OF POLYOCTENAMER USING 1,9-DECADIENE AS A MONOMER.

The first high molecular weight polymer synthesized by acyclic diene metathesis polymerization is reported herein. Prior to the research discussed below, the catalyst requirements and the reaction conditions required to produce high molecular weight polymers by acyclic diene metathesis polymerization techniques were unknown. Following the successful metathesis of styrene and its derivatives, the focus of the research turned toward the polymerization of 1,9-decadiene to demonstrate that acyclic diene metathesis (ADMET) could produce high molecular weight polyoctenamer.

Polyoctenamer was chosen as a target model polymer since it is well characterized [78]. The physical properties of polyoctenamer prepared by ring opening metathesis polymerization are known [78]; thus it was possible to compare the properties of acyclic diene metathesis polymerization samples directly with polymers formed by ring opening metathesis polymerization.

Eight polymerizations were performed to establish the most suitable conditions to yield high molecular weight polymers, and to investigate the different properties of the polyoctenamer samples produced. A discussion of the molecular weights obtained under different experimental conditions, as well as the physical properties of the polymers formed, follows.

Acyclic Diene Metathesis as a Polymerization Reaction

The polymerization chemistry under investigation (Figure 4-1) yields only two products, polyoctenamer and ethylene, and by removing ethylene the polymerization could be driven to produce high molecular weight polyoctenamer. No accompanying reactions were observed. The first four reactions specifically were done to show that high molecular weight polyoctenamer can be produced by ADMET polymerization (Table 4-1).

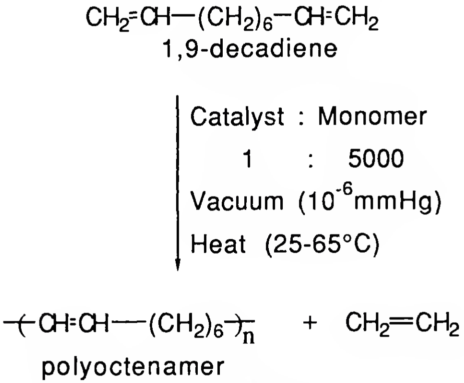


Figure 4-1. Acyclic Diene Metathesis Polymerization of 1,9-decadiene.

Table 4-1. Molecular weights of first four polyoctenamer samples prepared by acyclic diene metathesis polymerization

Polyoctenamer Reaction	Viscosity[a] (dL/g)	Molecular Weight ($\overline{Mn}$)
1	—	1 700[b]
2	0.26	11 000[b] 12 000[c]
3	—	1 600[b]
4	0.89	57 000[d]

(a) 25°C in toluene; (b) Endgroup analysis by ^{13}C NMR; (c) $\overline{M}_n$ by VPO analysis; (d) $\overline{M}_w$ (108000) and $\overline{M}_n$ were measured assuming the polymer to be polystyrene, the calibration standard, and multiplied by 0.45. This factor is the estimated ratio of the unperturbed dimensions, $<L_o^2/M>$, for polystyrene and polyoctenamer.

Three additions of catalyst were made, and a large volume of solvent was used in the first reaction. While a low molecular weight (1700) pure polyoctenamer sample with a trans content of 65% was produced in the first reaction, it was encouraging that no intractable material was observed. The low molecular weight of the polymer is attributed to the oligomers solidifying in the breakseal ampules (Figure 2-7, page 37) that contained the catalyst and monomer, which prevented metathesis. Thus, oligomers were prevented from constant contact with the catalyst thereby reducing polymerization rates and allowing only the formation of oligomeric material.

Placing the monomer and catalyst ampules above the reflux condenser prevented the precipitation of polymer in the breakseal ampules. An increase in both the molecular weight and trans stereochemistry percentage of the product produced in the second polymerization reaction was achieved. More efficient refluxing and return of the unreacted monomer and solvent to the reaction vessel could increase the molecular weight and simultaneously decrease the reaction time.

When large volumes of solvent are used, it becomes evident from reaction 3 that only low molecular weight oligomers with a low stereochemical trans content are formed. In light of Reaction 3 results, it seems as if higher temperatures and a minimal amount of solvent could produce the desired high molecular weight polymers.

A minimal amount of solvent and reaction temperature of 55°C produced a polymer of high molecular weight and high percentage trans stereochemistry. Based on the results of Reaction 4, acyclic diene metathesis (ADMET) polymerization can produce high molecular weight polyoctenamer. Experiments followed in which different reaction conditions were examined.

Table 4-2. Molecular weights of polyoctenamer samples produced under bulk acyclic diene metathesis polymerization conditions.

Reaction	% trans[a]	Molecular weight ($\bar{M}n$)
5	85	3000[b]
6	90	2000[b]
7	91	25000[c]

(a) As determined by quantitative ^{13}C NMR; (b) Endgroup analysis utilizing ^{13}C NMR; (c) $\bar{M}_n$ determined by VPO.

Bulk Polymerization Conditions

Bulk polymerizations are the most common method used for step polymerization since they yield fast reactions which can easily be controlled.

Bulk polymerizations [68]. are performed generally above the melting point of the polymer to facilitate agitation. Calderon [79] reported that 100% trans polyoctenamer melts at 73°C, and so a polymerization temperature of 75°C was chosen for the first bulk polymerization (Reaction 5, Table 4-2). A fraction of the product formed at 75°C was soluble in boiling benzene and had a low number average molecular weight.

Two additional reactions were performed under bulk polymerization conditions. Reaction 6 was allowed to proceed for 20 minutes at 25°C under bulk reaction conditions and a low molecular weight, 91% trans polyoctenamer resulted. No intractable material was produced indicating that no side reactions occurred at the lower temperature.

Effective agitation of polyoctenamer samples formed under bulk conditions at 25°C becomes impossible after approximately one half hour due to the increased viscosity of the reaction product. By raising the reaction temperature to 55°C, it was possible to reduce the viscosity of the sample and magnetic agitation again became possible. However, after an additional four hours, the polymer's viscosity increased to the point where magnetic agitation ceased. These manipulations increased the molecular weight to a value of 25000. The increased molecular weight observed in reaction 7 indicates that polyoctenamer can successfully be prepared by acyclic diene metathesis polymerization under bulk reaction conditions at 55 °C.

Higher molecular weights can be achieved in shorter times with agitation from high torque mechanical stirring. Results from bulk polymerizations indicated that the catalyst does not decompose at 55 °C. A polymer of high trans stereochemistry (approximately 90%) with moderate molecular weight can be produced in a relatively short time under bulk conditions. Better agitation undoubtedly will produce even higher molecular weights.

Tailoring of Acyclic Diene Metathesis Formed Polymers

The ability to tailor acyclic diene metathesis polymerization reaction conditions to produce a wide variety of polymers with varying molecular weights and physical properties (e.g., melting and crystallization points) was investigated in this experiment. Termination of acyclic diene metathesis polymerization is achieved by exposing the polymerization to oxygen and moisture, which decomposes the catalyst. Because the catalyst is not permanently fixed to the chain ends, both chain ends of the polymer retain vinyl bonds that can be further polymerized by acyclic diene metathesis techniques if the polymer is to be reacted with active catalyst (Figure 4-2).

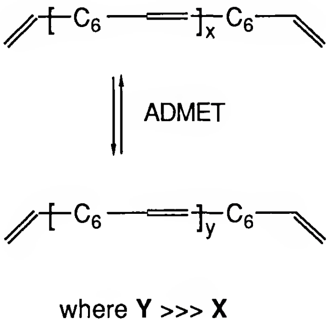


Figure 4-2. Continued telechelomer ADMET polymerization to high molecular weight polyoctenamer.

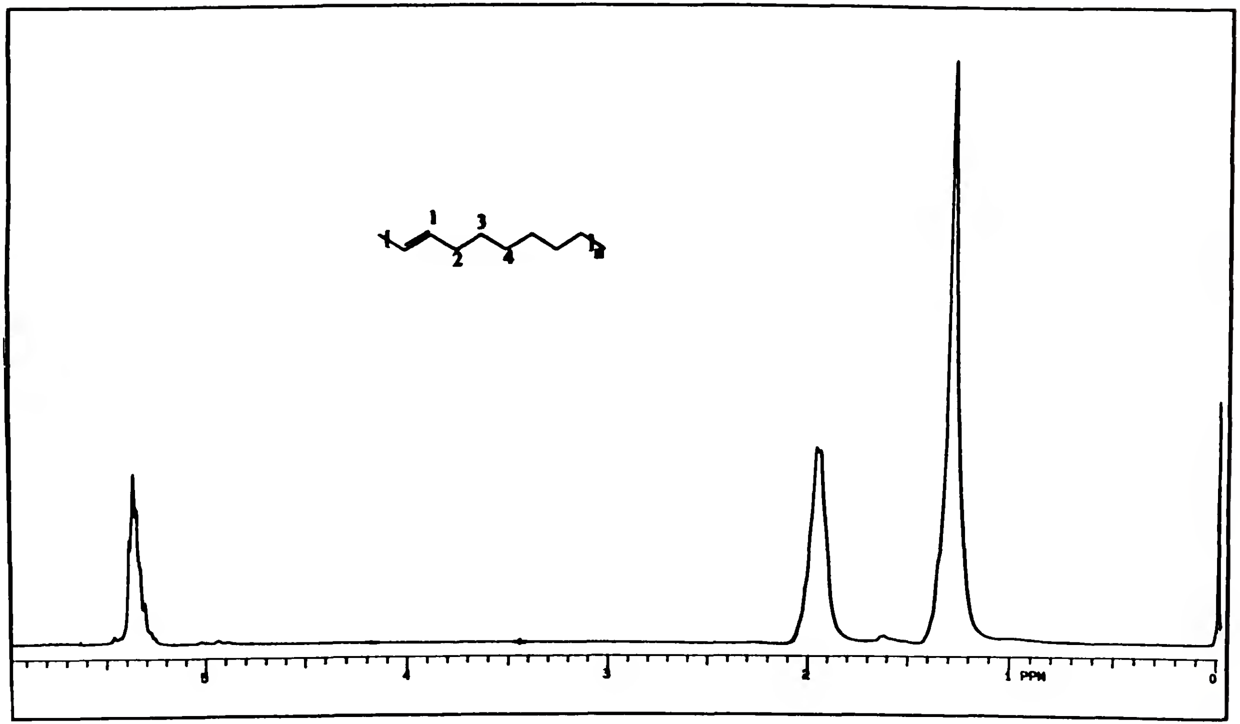
A polyoctenamer sample that had a reduced viscosity of 0.26 dL/g was converted to a higher molecular weight polymer, as indicated by an increased reduced viscosity number of 0.76 dL/g. The trans olefin content increased from 78% to 88% which resulted in higher melting and crystallization points for the produced polymer.

Acyclic diene metathesis polymerization eliminates the possibility of producing a polymer with undesirable physical properties, provided these properties can be altered by an increase in molecular weight. The ability to increase the molecular weight of a sample and tailor its physical properties indicates the advantage that acyclic diene metathesis polymerization has over other polymerization techniques.

Determining the Stereochemistry of the Olefin Units in Polyoctenamer

The stereochemistry of the internal olefin units of polyoctenamer varies [78], depending on the method and reaction conditions used to produce the polymer sample. Because the physical properties of a specific polyoctenamer sample depend on the stereochemistry of the internal olefin units, it is important that the cis/trans ratio of the internal olefin units be determined accurately. Three spectroscopic techniques can used to determine the cis and trans stereochemistry, ^1H NMR, ^{13}C NMR and infrared spectroscopy. All three methods were employed to characterize the polymer samples that are described in this dissertation and the accuracy of the cis/trans ratios assigned by these methods was individually accessed.

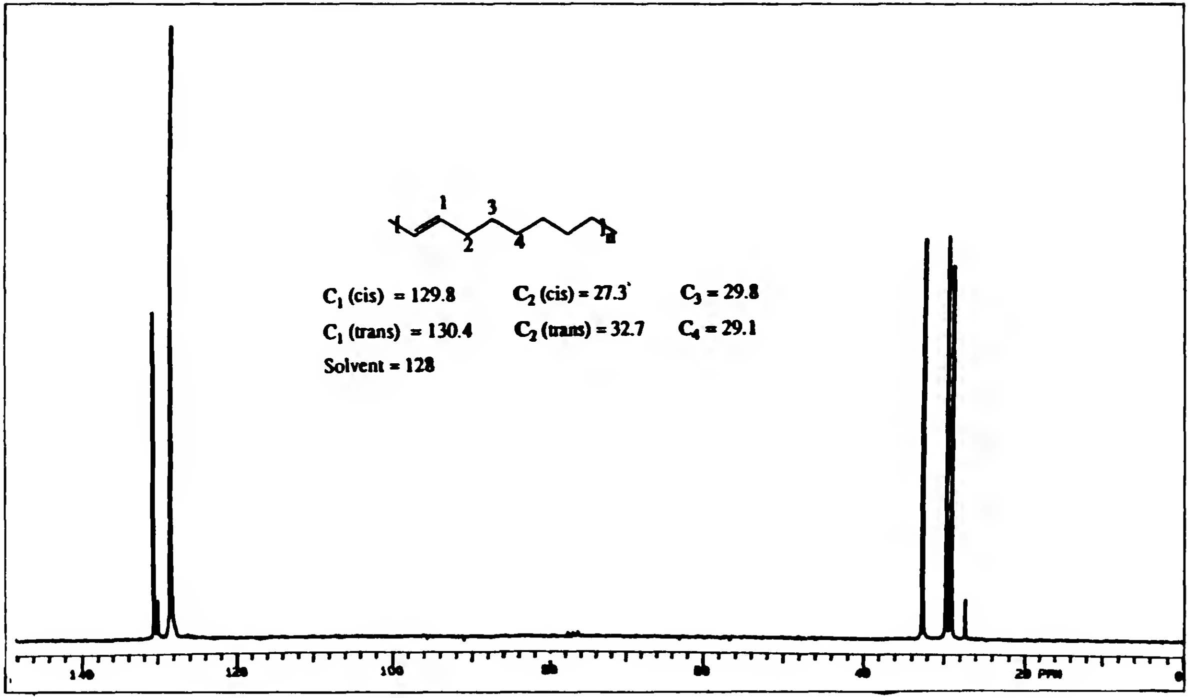
The proton NMR spectra for all of the polymer.samples prepared by acyclic diene metathesis essentially were identical (Spectrum 4-1), with the exception of cis/trans ratios. Hatada [80,



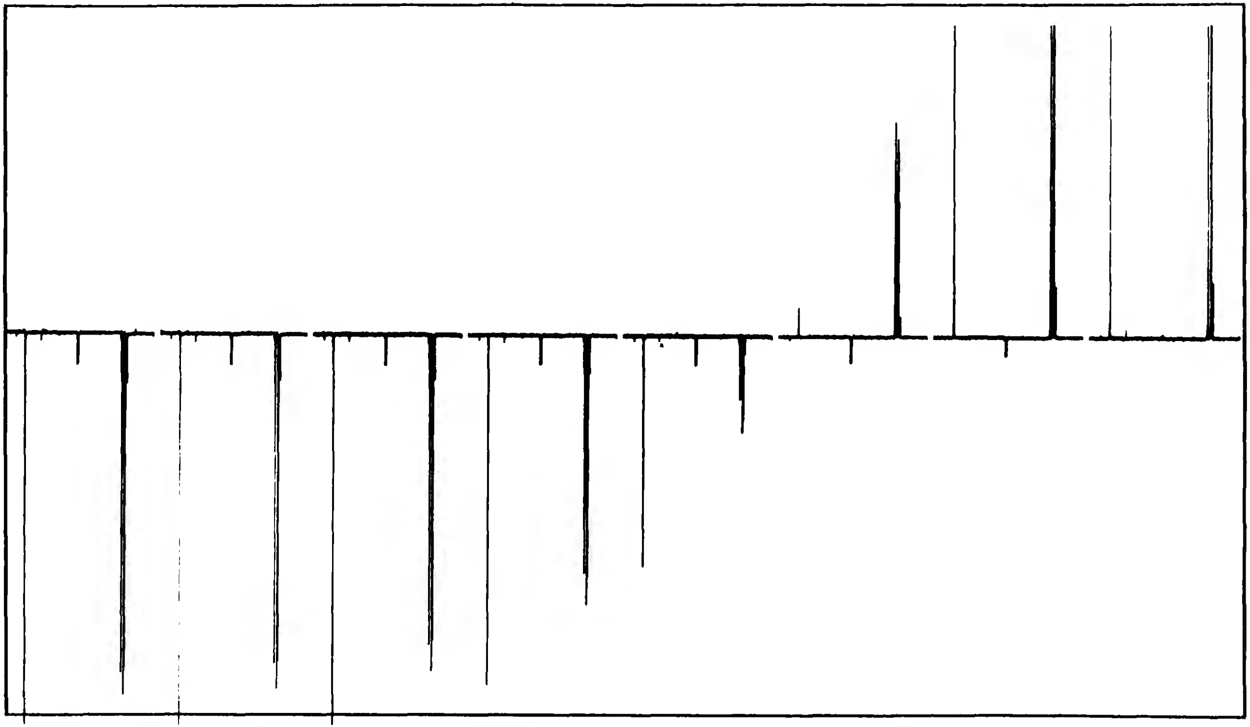
Spectrum 4-1. 200 MHz ^{1}H NMR of linear polyoctenamer produced by ADMET polymerization of 1,9-decadiene.

81] used spin decoupling to distinguish between the cis and trans proton signals of 1,4-polybutadiene, a technique which can be applied to polyoctenamer. Spin decoupling was applied to polyoctenamer by Sato [82], whereby the olefinic protons of polyoctenamer can be separated into cis and trans peaks. However, the use of quantitative ^{13}C NMR would lead to much more accurate assignment of cis/trans ratios for polyoctenamer, because the separation between the two decoupled proton NMR peaks, is minimal (only 0.5 ppm without baseline separation). A comparison of the ^{13}C NMR resonances for polyoctenamer reported by Katz [83] and those found for the polyoctenamer samples prepared by acyclic diene metathesis polymerization indicates that only linear polyoctenamer is produced (Spectrum 4-2).

Prior to performing any quantitative ^{13}C NMR experiments, the T_1 relaxation times of all the carbon atoms present in a repeat unit of polyoctenamer were determined with a Varian XL 200 spectrometer [84]. Reliable carbon integrations can only be obtained from fully relaxed ^{13}C NMR spectra [85], and relaxation times were measured for 3 different polyoctenamer samples in order to determine the longest T_1 present in a repeating unit. Spectrum 4-3 indicates the 8 different relaxation times used and the effect of the relaxation times on the signals of the different carbon atoms in a repeat unit. The T_1 relaxation times found for the 8 carbon atoms in a repeat unit are listed in Table 4-3.



Spectrum 4-2. 50 MHz ^{13}C NMR of linear polyoctenamer produced by ADMET polymerization of 1,9-decadiene.



Spectrum 4-3. 50 MHz ^{13}C NMR of linear polyoctenamer, produced by ADMET polymerization, showing the effect of eight different T1 relaxation times on the intensity of the various signals.

Table 4-3. Relaxation times of carbon atoms in a repeat unit of polyoctenamer.

Peak(ppm)	T_1(sec.)	Error(sec.)
139.1	10.42	2.73
130.3	1.99	0.03
129.9	1.49	0.15
114.1	4.89	0.95
32.7	0.99	0.02
29.6	1.15	0.02
29.2	1.27	0.14
29.0	1.13	0.02
27.2	1.21	0.11

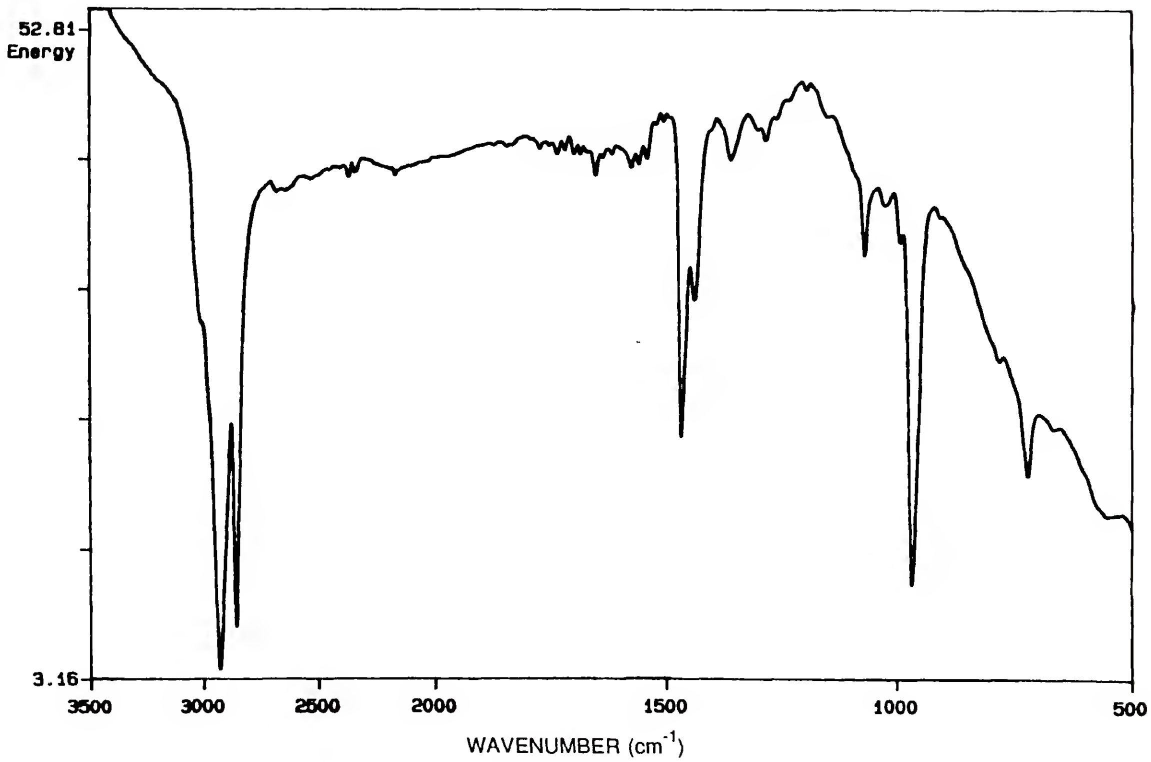
Based on this information, a single pulse delay mode and delay times more than four times that of the longest T_1 were used for quantitative carbon experiments.

Using ^{13}C NMR spectroscopy, it is possible to distinguish between both the cis and trans internal olefin carbons and the allylic carbon adjacent to the internal olefin carbon. The internal cis olefin carbon appears at l29.8 ppm and the trans internal olefinic appears at l30.4 ppm. Several researchers [86, 87, 88, 89, 90, 91] have demonstrated that the carbon atom adjacent to the internal olefinic carbon has two different resonances, (i.e., the cis carbon at 27.3 ppm and the trans carbon at 32.7 ppm). The resonances at 32.7 ppm were reported to be weak or unobserved for the predominantly cis-polyoctenamers produced by ring opening metathesis. A one to one correlation between the peak intensities of these allylic carbon resonances and those of the internal olefin carbons corroborates the assignment of percentage trans stereochemistry for a specific polymer sample. The percentage trans stereochemistry, as determined by quantitative carbon NMR, of polyoctenamer samples prepared by acyclic diene metathesis polymerization is summarized in Table 4-4, page 97.

On occasion, cis and trans stereochemistry can be determined by infrared spectroscopy; however, this is difficult for polyoctenamer. The FTIR spectrum (Spectrum 4-4) of polyoctenamer produced in reaction 3 illustrates the difficulties associated with assigning the percentage trans stereochemistry present in a polyoctenamer sample. A typical polyoctenamer sample has two absorption bands at 1404 and 970 cm^{-1} arising, respectively, from in-plane bending of the cis unit and out-of-plane deformation of the trans unit; however, a strong methylene scissoring absorption band at 1470 cm^{-1} makes it difficult to separate the trans absorption band properly [92]. Due to this overlapping of trans absorptions.

Effects of Percentage Trans Stereochemistry on Melting and Crystallization Temperatures of Polyoctenamer

Calderon first reported that a linear relationship exists between the percent trans stereochemistry and the melting point of a specific polyoctenamer sample prepared by ring opening metathesis. [79]. It is of great interest to determine whether polyoctenamer samples prepared by acyclic diene metathesis polymerization possess the same thermal characteristics as those samples produced by ring opening metathesis polymerization.



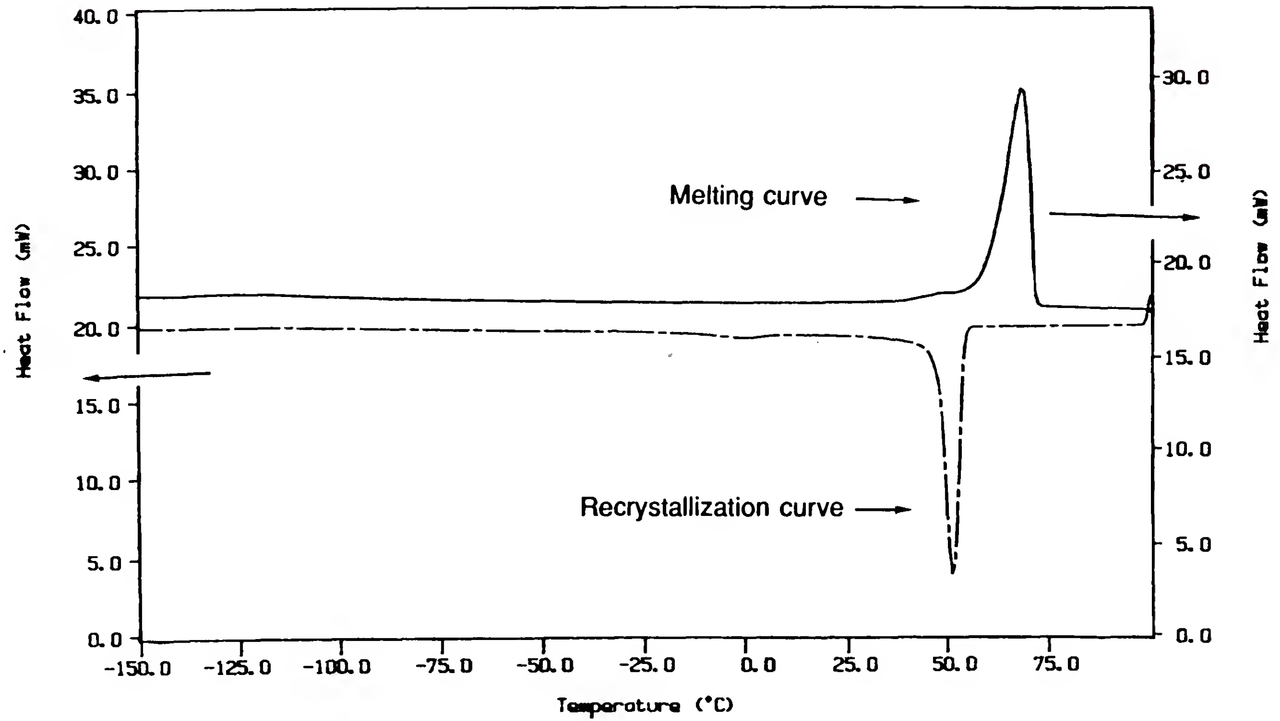
Spectrum 4-4. Infrared spectrum of linear polyoctenamer produced by ADMET polymerization of 1,9-decadiene.

Using differential scanning calorimetry, the polyoctenamer samples described previously were subjected to repeated heating and cooling cycles. Unlike Calderon, who detected a dependence on thermal history for ROMP polyoctenamer [79], no dependence on previous thermal histories was observed for ADMET polyoctenamer. After these ADMET samples were quenched, identical melting points were observed as before (Spectrum 4-5) which indicates that the ADMET polymers melt and crystallize at specific temperatures independent of previous thermal histories.

Using Equation 4-1, Calderon [79] predicted that 100% trans polyoctenamer would have a melting point of 73 ± 2°C and Flory [93] has shown that Equation 4-1 applies to the melting point of any co-polymer having randomly placed crystallizable repeat (Type T) and noncrystallizable (Type C) repeat units,

$$(1/T_m) - (1/T_m^o) = -(R/\Delta H_u) \text{ Ln } N_t \qquad 4\text{-}1$$

where N_t is the mole fraction of repeat units of type T; T_m^o is the melting point when $N_t = 1$; Tm is the melting point for any given value of N_t; ΔH_u is the heat of fusion per mole of repeat unit of type T; and R is the universal gas constant. In the case of polyoctenamer, Flory's theory assumes a random distribution of crystallizable trans-olefin units (Type T) and noncrystallizable cis-olefin units (Type C).



Spectrum 4-5. Differential scanning calorimetry data of linear polyoctenamer produced by ADMET polymerization of 1,9-decadiene

Polyoctenamer samples prepared by acyclic diene metathesis exhibit a linear relationship between melting point and percentage trans olefin units (Figure 4-3). The data used to construct Figure 4-4 is listed in Table 4-4.

Table 4-4. Melting and crystallization temperatures of polyoctenamer samples prepared by acyclic diene metathesis polymerization.

Reaction	% trans	Melting point (°C)	Crystalization Point (°C)
PO	77	52.0	31.6
2	80	55.7	36.8
6	85	57.1	41.7
5	88	63.5	44.2
8	90	66.3	52.3
7	91	67.6	54.1
4	93	69.2	56.8

PO being a polyoctenamer sample prepared by means of ring opening metathesis polymerization.

Using these data, a theoretical maximum melting point of 77°C ±1°C is calculated from the intercept of the line shown in Figure 4-3, which is 4°C higher than Calderon predicted. The difference can be attributed to limitations in the accuracy of the methods and instrumentation used by Calderon; not to a difference in polymer properties. Utilizing quantitative ^{13}C NMR (i.e., integration of peaks that are separated by 5 ppm) is more accurate in assigning the percent trans stereochemistry present in polyoctenamer than IR or

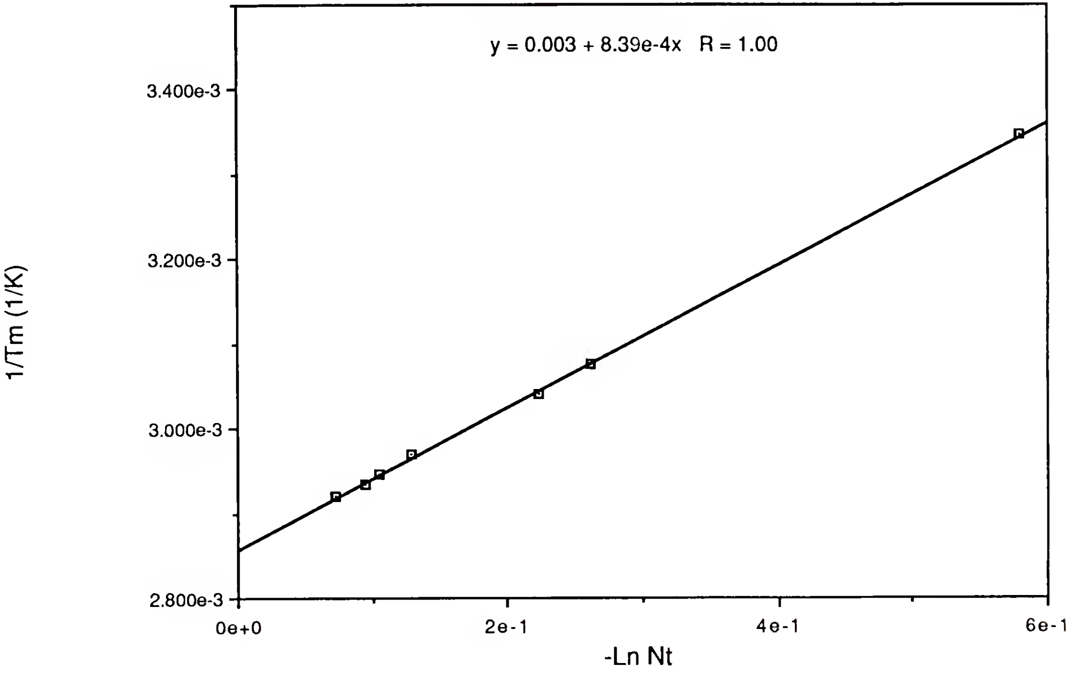


Figure 4-3. Linear relationship between $1/T_m$ and -Ln Nt for elucidation of the melting point of 100% trans polyoctenamer.

^{1}H NMR methods. To insure high accuracy, the melting points were determined using a Perkin Elmer 7500 differential scanning calorimetry system that have both an accuracy and precision of ± 0.1°C. The instrument was calibrated repeatedly by a two point method and standards that bracketed the melting range of the polymer samples. Two commercial samples of polyoctenamer, Vestanamer 8012™ and Vestanamer 6213™, also fall on the same line as the polymer samples prepared by acyclic diene metathesis polymerization. The commercial polymers were produced using ring opening metathesis procedures [78], similar to those utilized by Calderon.

The molar heat of fusion (ΔHu) of the trans olefinic repeat unit can be calculated from the slope of the line in Figure 4-3. The least-squares value obtained for the heat of fusion was 2368 cal./mole with a 95% confidence limits of ± 20 cal./mole. The entropy of fusion $Hu/T_m{}^\circ$ was 6.8 cal./mole-deg. Again, the difference between these results and that of Calderon is attributed to analysis error and not a difference in polymer composition.

The polyoctenamer samples produced by acyclic diene metathesis have a high percentage trans stereochemistry which is in contrast to polyoctenamer produced by ring opening metathesis polymerization.

The recrystallization temperature of polyoctenamer can also be related to the percent trans stereochemistry of the polymer, a point that has not been made before. Recrystallization temperatures of polyoctenamer produced by acyclic diene metathesis are independent of their thermal histories, and thus it is possible to predict recrystallization temperatures relative to the percentage trans stereochemistry of the sample. This is in contrast with the recrystallization temperatures of ring opening metathesis polymerization polyoctenamer, which exhibit dependence on previous thermal history [79] due to low percent trans stereo chemistry. The variations in recrystallization temperatures previously made it impossible to predict recrystallization points relative to percentage trans stereochemistry for ROMP polyoctenamer samples [79].

Utilizing differential scanning calorimetry, it was possible to accurately determine the recrystallization temperatures of samples produced by acyclic diene metathesis polymerization as well as the higher trans commercial ring opening metathesis polymerization sample, Vestenamer 8012™ (Table 4-4, page 97). Using Equation 4-1 and plotting $1/T_C$ vs.-Ln Nt, a linear relationship between the two variables was established. From the intercept of the line (Figure 4-4) a recrystallization temperature of 58 ± 2°C for 100% trans polyoctenamer can be predicted.

Determination of the Molecular Weights of the Polyoctenamer Samples Produced by Acyclic Diene Metathesis Polymerization

Since the physical properties of any polymer depend on its molecular weight, it is essential to be able to accurately determine this quantity.

Very few methods exist which directly determine the molecular weight of a polymer sample. Most instrumental methods produce comparison molecular weights (i.e., the molecular weight of an unknown sample is determined by comparing it to several samples

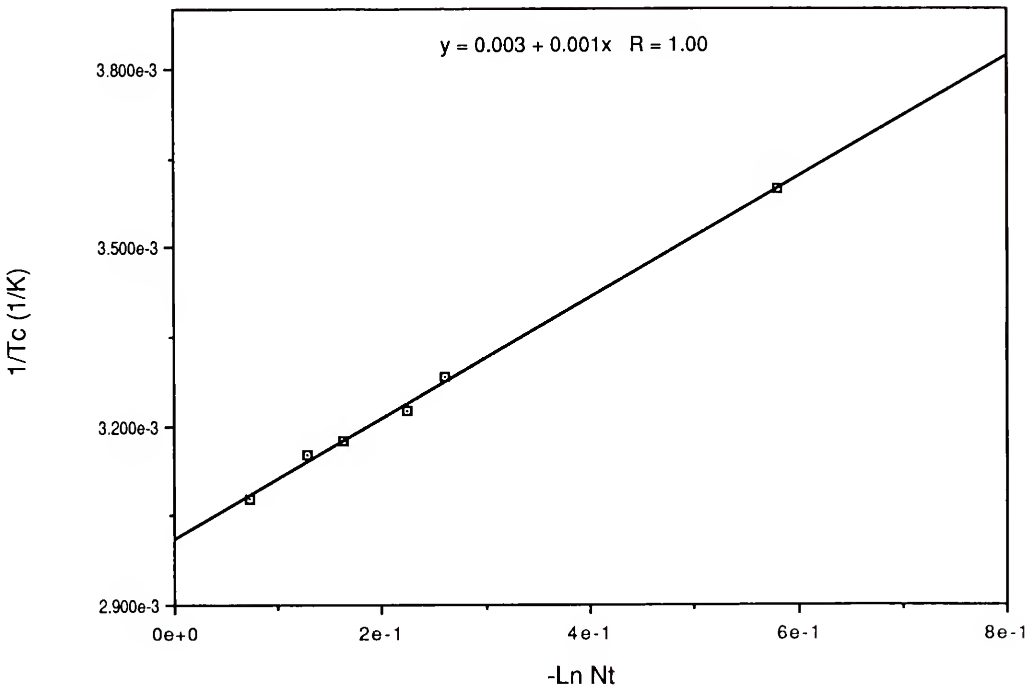


Figure 4-4. Linear relationship between $1/T_C$ and -Ln Nt for elucidation of the crystallization point of 100% trans polyoctenamer.

of known molecular weight). More often than not, the unknown molecular weight polymer and standardized molecular weight polymers have different repeating units (i.e., not the same chemical structure).

Several mathematical relationships exist which correlate the physical properties of a polymer sample with its influence on the molecular weight of a sample [94]. The viscosity molecular weight (Equation 4-3) is one such relationship that corrects for the changes in physical properties

$$\mathrm{Ln}\,[n] = \mathrm{Ln}\,K + a\,\mathrm{Ln}\,[\overline{Mv}] \qquad 4\text{-}3$$

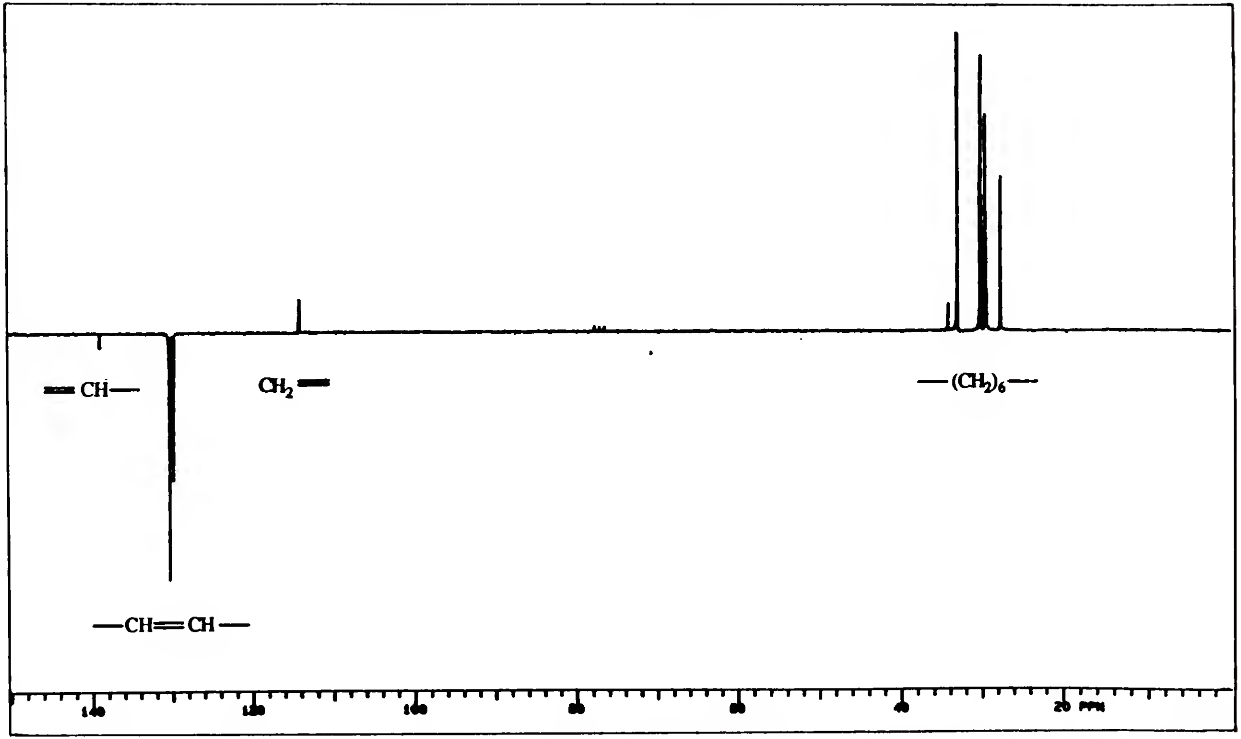
by using the the Mark-Howink-Sakurada constants, "K" and "a". Without these constants, only relative molecular weight comparisons can be made between different samples of the same type of polymer. Consequently, it is important to know the Mark-Howink-Sakurada constants for any polymer. These constants, which were unknown for polyoctenamer, have been determined in the course of this work.

There exist several different methods for the determination of the molecular weight of a polymer sample. Employing several different molecular weight determination techniques, values for the "K" and "a" were calculated for polyoctenamer samples having molecular weights in the range 10^3 - 10^5.

Since the Mark Howink Sakurada constants of polyoctenamer at 25°C using toluene as solvent were unknown, the intrinsic viscosities determined could not be converted to molecular weights using equation 4-3. Estimated Mark-Howink-Sakurada constants were calculated from the molecular weights determined by NMR endgroup and/or vapor pressure osmometry analysis for polymers produced in two separate experiments. The molecular weights needed for these calculations were determined as described below.

It is possible to detect the vinyl endgroups of low molecular weight polyoctenamer samples produced by acyclic diene metathesis polymerization by ^{13}C NMR spectroscopy (Spectrum 4-6). Number average molecular weights ranging from 1700 to 11 000 were determined by 13C NMR endgroup analysis for ADMET polyoctenamer (Table 4-1, Page 82 and Table 4-2, page 84). This opportunity does not always exist in ring opening metathesis polymerization since the ROMP polymers possess an unknown chain capping group on the termination end and the alkylediene ligand, initially present on the catalyst, on the initiation end.

In order to verify these number average molecular weights obtained by endgroup analysis, the molecular weights of polyoctenamer samples produced in two separate experiments were determined by vapor pressure osmometry. Sucrose octaacetate (MW = 678.6) was used to calibrate the vapor pressure osmometer at 51°C using toluene as solvent, and a calibration factor K of 6705 was obtained which is in good correlation with the value of 6510 reported by the manufacturer [95] of the instrument (Figure 4-5). A number average molecular weight of 12 000 (Figure 4-6) was obtained for one sample which is in excellent agreement with the value of 11 000 found by NMR endgroup analysis. A second polymer sample produced a VPO value of 25 000 (Figure 4-7).



Spectrum 4-6. 50 MHz ^{13}C NMR (attached proton test) of low molecular weight polyoctenamer produced by ADMET polymerization of 1,9-decadiene.

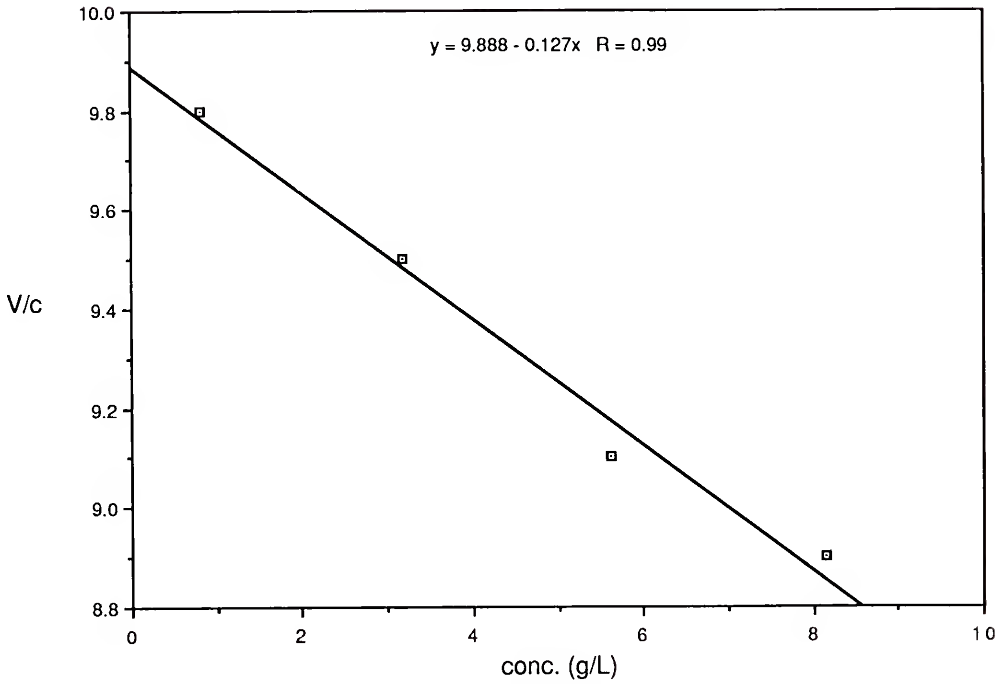


Figure 4-5. Vapor pressure osmometer calibration curve using sucrose octaacetate as the standard.

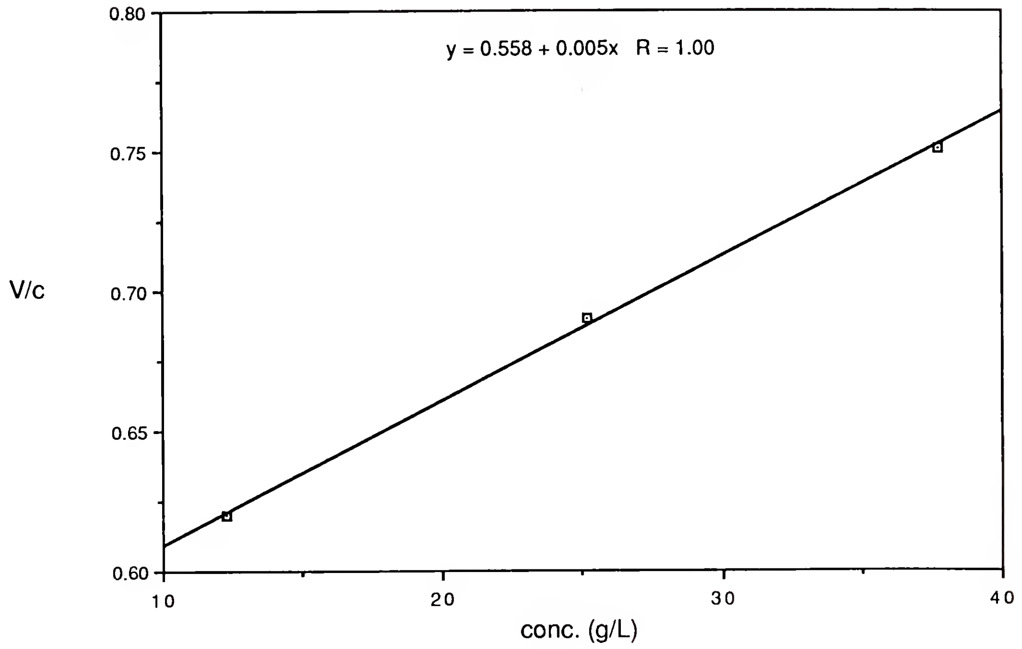


Figure 4-6. Vapor pressure osmometry data of polyoctenamer produced in reaction 2 by ADMET polymerization. The Mn is 12000

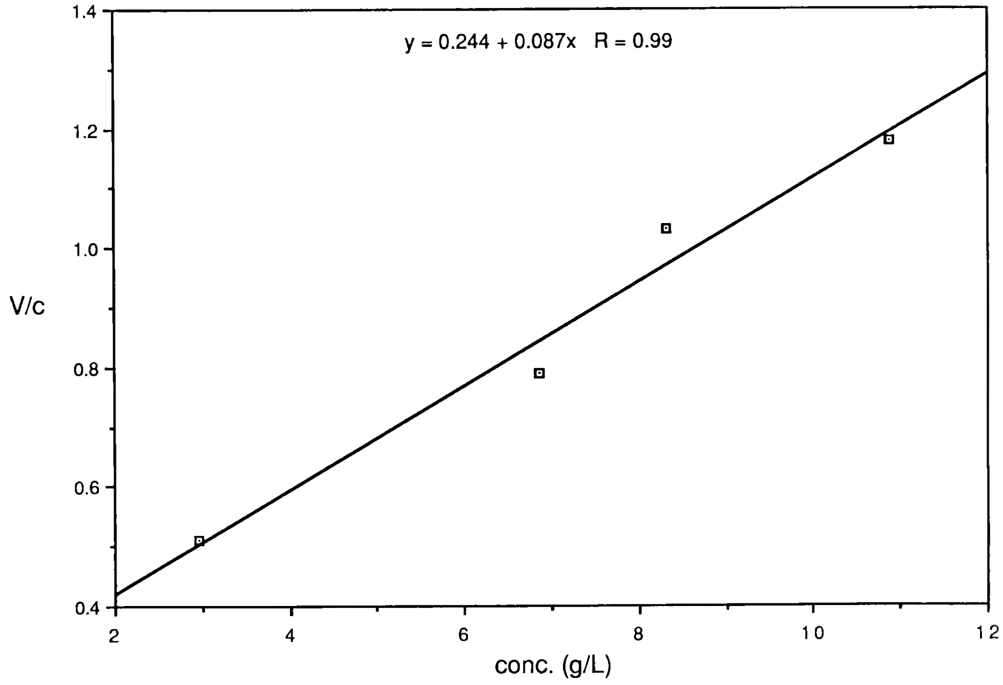


Figure 4-7. Vapor pressure osmometry data of polyoctenamer produced in reaction 8 by ADMET polymerization. The Mn is 25000

Determination of the Mark-Howink-Sakurada Constants, "K" and "a", for Polyoctenamer at 25°C in Toluene

The most widely used method of determining the Mark-Howink-Sakurada constants, employs very narrow molecular weight fractionated polymer samples [96], where molecular weight is determined using absolute methods such as light scattering or osmometry. Fractionation is done to ensure very narrow molecular weight uniformity, ($\overline{Mw}/\overline{Mn}$ = 1, for which $\overline{Mw}$ = $\overline{Mn}$ = $\overline{Mv}$ provides a good approximation). The light scattering molecular weight ($\overline{Mw}$) or osmometry molecular weight ($\overline{Mn}$) now can be used to solve the viscosity molecular weight (Equation 4-3) since these molecular weights are virtually equivalent when the polydispersity ratio approaches unity.

One important class of polymers which constitutes an exception to the restriction of narrow molecular weight distribution, consists of linear polyamides and polyesters polymerized under equilibrium conditions. For equilibrium condition samples the molecular weight uniformities are always random and

$$[n] = K\,\overline{Mn}^{a} \qquad 4\text{-}4$$

Equation 4-4 can be applied [96]. For this group (in which $\overline{Mw}$ = 2 $\overline{Mn}$) whole polymer samples can be used in calculations.

Acyclic diene metathesis polymerization is an example of an equilibrium polymerization and should lead to molecular weight uniformities approximating 2, and therefore, the polyoctenamer samples produced by acyclic diene metathesis polymerization fall into the category of equilibrium polymers. Thus equation 4-4 can be applied. Mark-Howink-Sakurada constants are not strictly independent of the molecular weight range over which they are determined. Oligomers (less than about 100 repeating units in most vinyl polymers) often conform to Equation 4-5,

$$[n] = K\overline{M}v^{0.5} \tag{4-5}$$

where "K" and the exponent "a" are independent of the solvent [96]. Since solvent independence is assumed, ie., a theta solvent, the "a" value for the ideal statistical coil is 0.5 and applies to these oligomers.

Absolute molecular weights of polyoctenamer samples produced in two acyclic diene metathesis polymerizations were determined, as well as the intrinsic viscosities of both polymer samples and Mark-Howink-Sakurada constants for polyoctenamer were calculated using equation 4-3. A "K" value of 1.46×10^{-3} and an exponent "a" of 0.552 were obtained from these calculations. Both polymers fall in the 10^3 -10^5 molecular weight range which is above the lower limit of calibration (100 repeating units). A value of close to 0.5 but slightly higher is expected since approximately ideal chain behavior is realistic for this molecular weight range in a good solvent.

Reduced viscosities of the polyoctenamer samples of higher molecular weight were determined by viscometry. Figures 4-8, 4-9, 4-10 and 4-11 show the plots of $[n]_{sp/c}$ and $[n]_{inh/c}$ versus

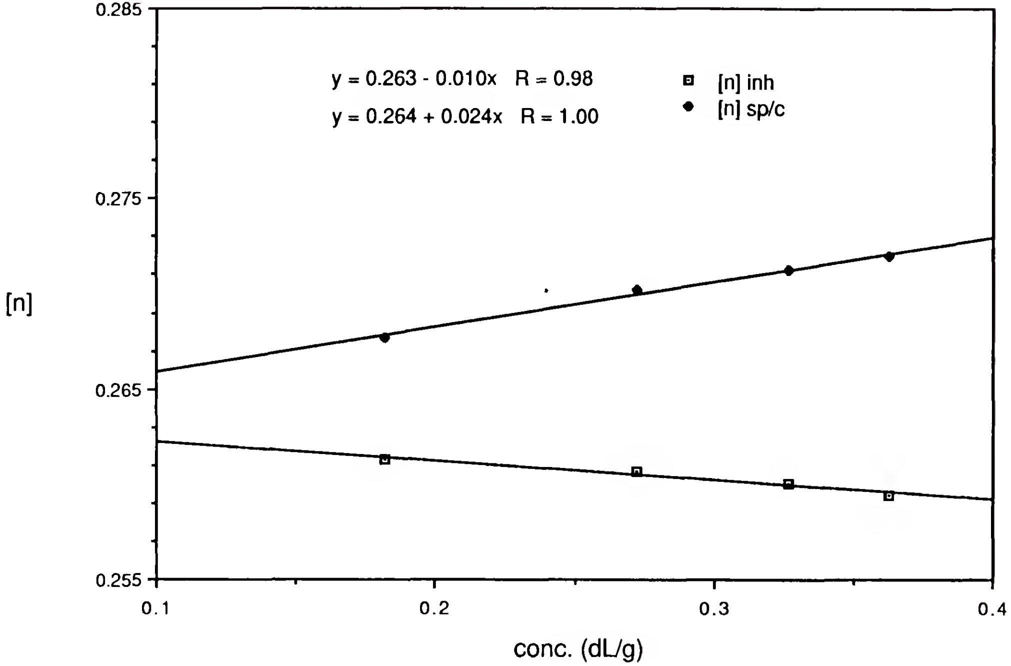


Figure 4-8. Viscosity of polyoctenamer produced in reaction 2 by ADMET polymerization.

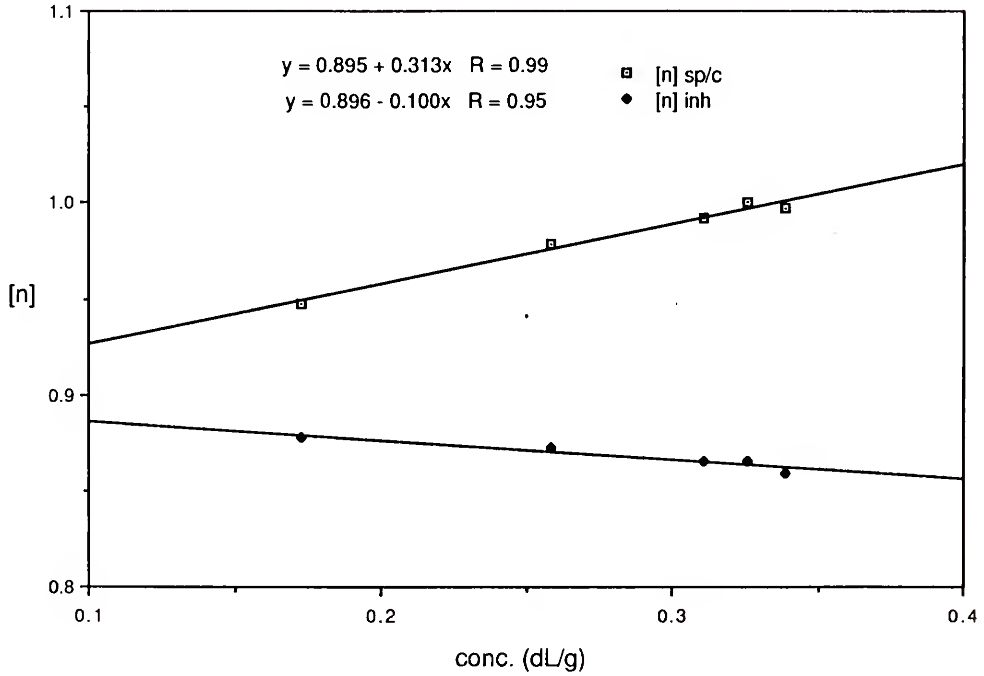


Figure 4-9. Viscosity of polyoctenamer produced in reaction 4 by ADMET polymerization.

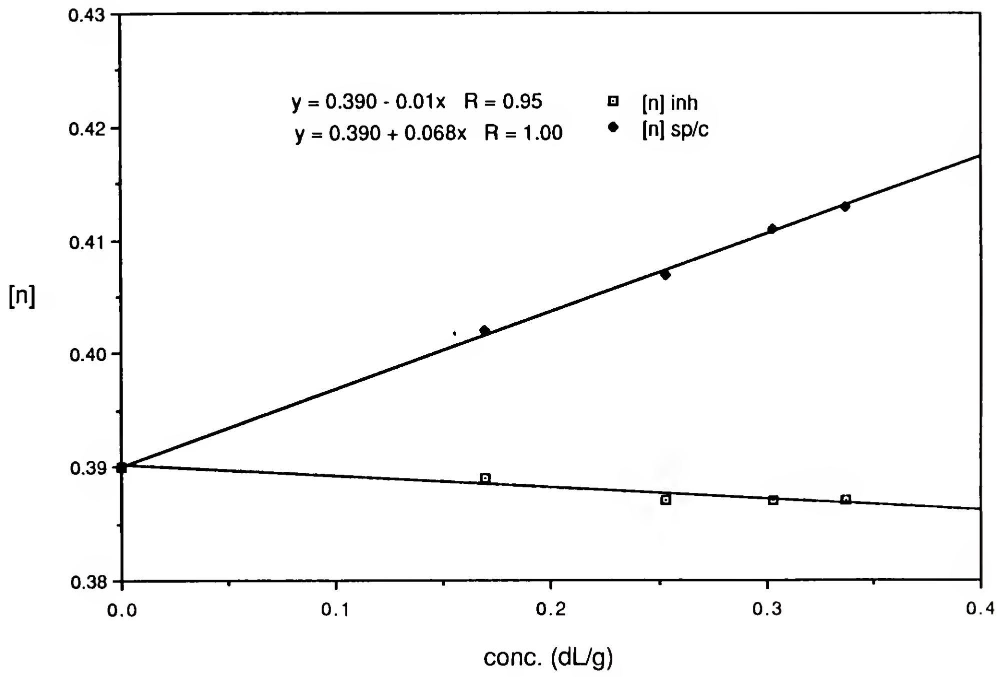


Figure 4-10. Viscosity of polyoctenamer produced in reaction 7 by ADMET polymerization.

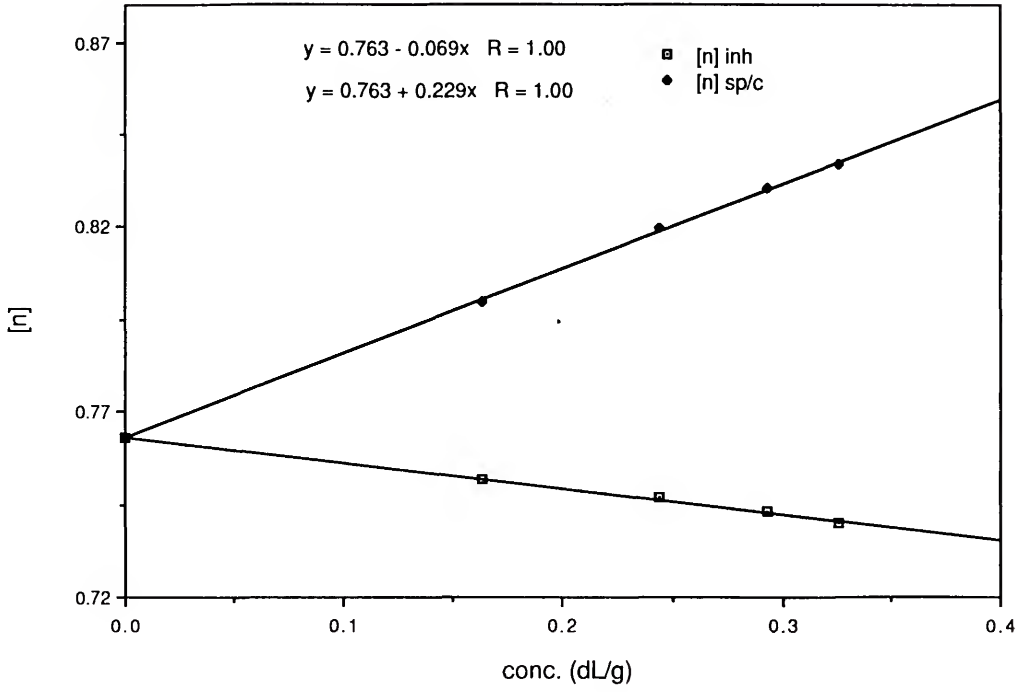


Figure 4-11. Viscosity of polyoctenamer produced in reaction 8 by ADMET polymerization.

concentration for four different samples. Reduced viscosities extrapolated from these figures are listed in the experimental section.

Size exclusion chromatography was also done to determine molecular weight, and the uniformity of ADMET polymer samples [95]. A three point calibration curve was constructed using polystyrene standards dissolved in toluene at room temperature (Figure 4-12). The polymer that formed when a minimal amount of solvent was used (Figure 4-13) was determined to have a $\overline{Mw}$= 239 000 and $\overline{Mn}$ = 127 000 according to polystyrene calibration. These are not polyoctenamer molecular weights and had to be converted. The universal calibration curve (Equation 4-2) proposed by J.V. Dawkins [97, 98]

$$\text{Log}\,\overline{Mp} = \text{Log}\,\overline{Mps} + \text{Log}\ Aps/Ap \qquad 4\text{-}2$$

was used to convert the above molecular weight values to actual polyoctenamer molecular weights. These "polystyrene" molecular weights can be converted to polyoctenamer molecular weights by multiplying by 0.45 [99] which represents the estimated ratio of the unperturbed dimensions ($A = <L_0^2>/M$) for polystyrene divided by that of polyoctenamer. Thus, the actual molecular weights of this, polyoctenamer sample is: $\overline{Mw}$ = 108 000 and $\overline{Mn}$ = 57 000. Molecular weights of this order of magnitude confirm that high molecular weight polyoctenamer can be produced by acyclic diene metathesis polymerization. The polyuniformity of the sample is 1.89 indicating that the sample was produced by a step propagation type

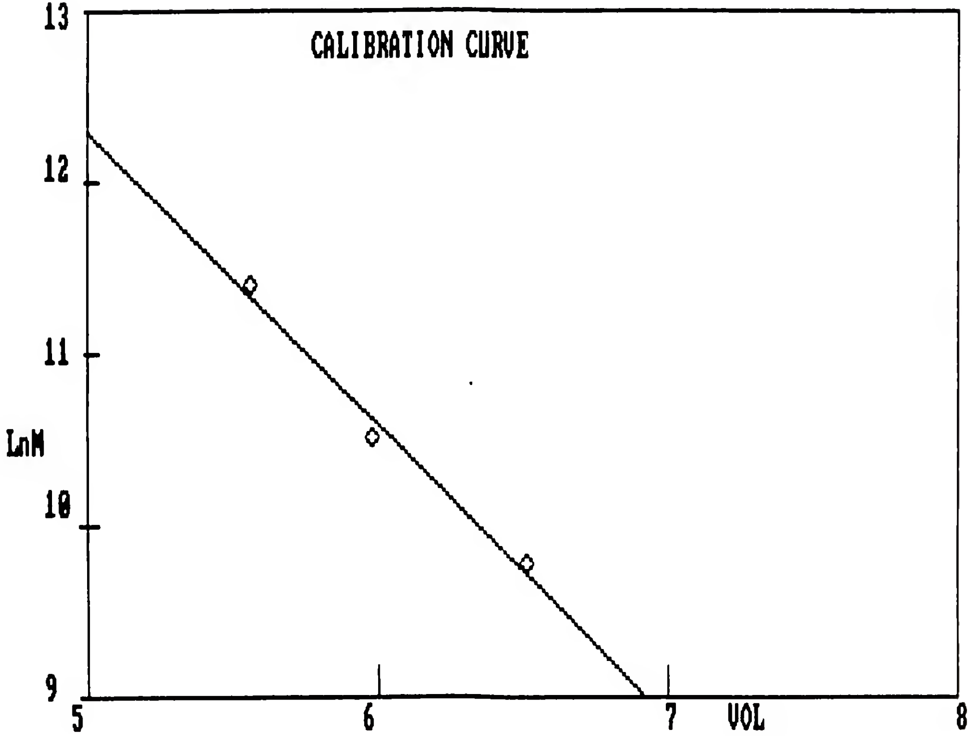


Figure 4-12. Size exclusion chromatography calibration curve using three polystyrene standards.

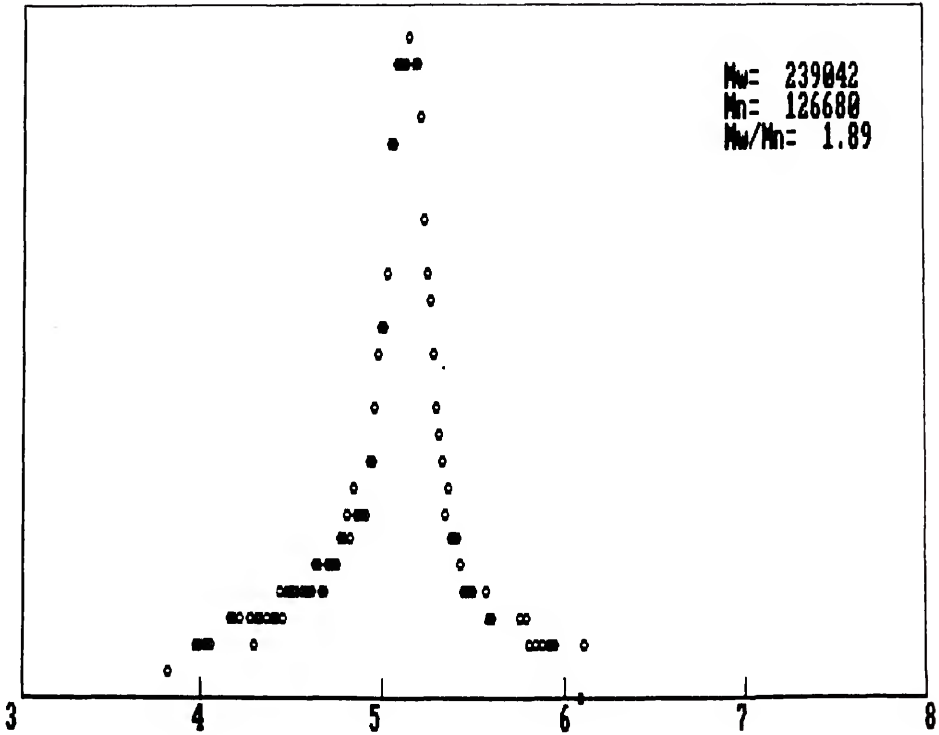


Figure 4-13. Size exclusion chromatography data of high molecular weight polyoctenamer produced by ADMET polymerization of 1,9-decadiene.

polymerization; which is expected in acyclic diene metathesis polymerizations.

Testing calculated Mark-Howink-Sakurada constants.

A test of the validity of the Mark-Howink-Sakurada constants lies in using them to calculate the molecular weight of the highest molecular weight sample prepared. Calculated MHS constants can be compared to the factor (0.45) used to convert the polystyrene molecular weights to polyoctenamer molecular weights. In doing so, it was found that the high molecular weight sample which has an intrinsic viscosity of 0.89, has a $\overline{Mv}$ of 110 000. The molecular weights obtained by size exclusion chromatography, $\overline{Mw}$ = 108 000 and $\overline{Mn}$ = 57 000, are in excellent correlation to what would be expected, i.e. $\overline{Mw} \geq \overline{Mv} >> \overline{Mn}$.

The validity of the assumptions previously made [97, 98] in using the universal calibration equation to convert polystyrene calibration molecular weights to polyoctenamer molecular weights by using a conversion factor of 0.45 [99] was confirmed. Additionally, for the first time, a reliable set of Mark-Howink-Sakurada constants for polyoctenamer has been measured.

Investigation of the Possible Formation of Macrocycles During Acyclic Diene Metathesis Polymerization

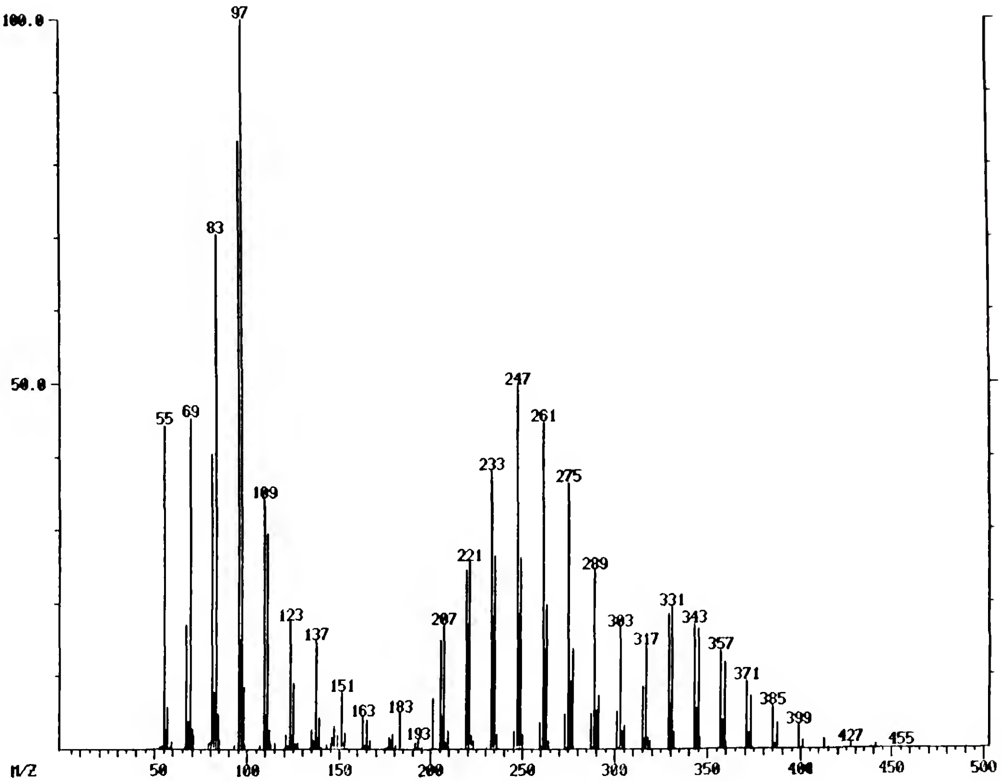
The ability of metathesis to produce both ring and linear compounds has had a great influence on its applicability as a polymerization reaction. As expected, the double bonds in a linear diene separated by 4 carbon atoms, metathesize to produce cyclohexene in 90% yields and no polymer is formed [100]. Cyclization metathesis is an example where the formation of a cyclic compound prevents metathesis from being used as a polymerization reaction. On the other hand, the ring opening of strained cyclic compounds by metathesis has proven to be an excellent polymerization technique [1].

Since metathesis chemistry is capable of yielding both cyclization and polymerization reactions, the possibility of acyclic diene metathesis polymerization of 1,9-decadiene being a combination of these two reactions was investigated. Acyclic diene metathesis might first cyclize the monomer, 1,9-decadiene, to cyclooctene which might subsequently ring open polymerize.

Kinetically, the probability of an oligomer reacting with its own chain end is low, because there is a high concentration of other diene molecules at the outset of the reaction. From an entropy perspective however, cyclization of 1,9-decadiene is favored since two molecules, cyclooctene and ethylene, are produced.

In order to examine the likelihood of cyclization, chemical ionization mass spectroscopy was performed on two well characterized polyoctenamer samples with similar number average molecular weights (~2000), one produced in 30 minutes under bulk reaction conditions, and the other produced in solution.

The mass spectrum (Spectrum 4-7) of the first sample showed parent ion peaks at m/e = 249 and 359, which is consistent with linear dimers and trimers (i.e., the vinyl endgroups are present) of polyoctenamer. Fractions of linear polyoctenamer (molecular weight



Spectrum 4-7. Chemical ionization mass spectrum of oligomers of polyoctenamer produced by ADMET polymerization of 1,9-decadiene.

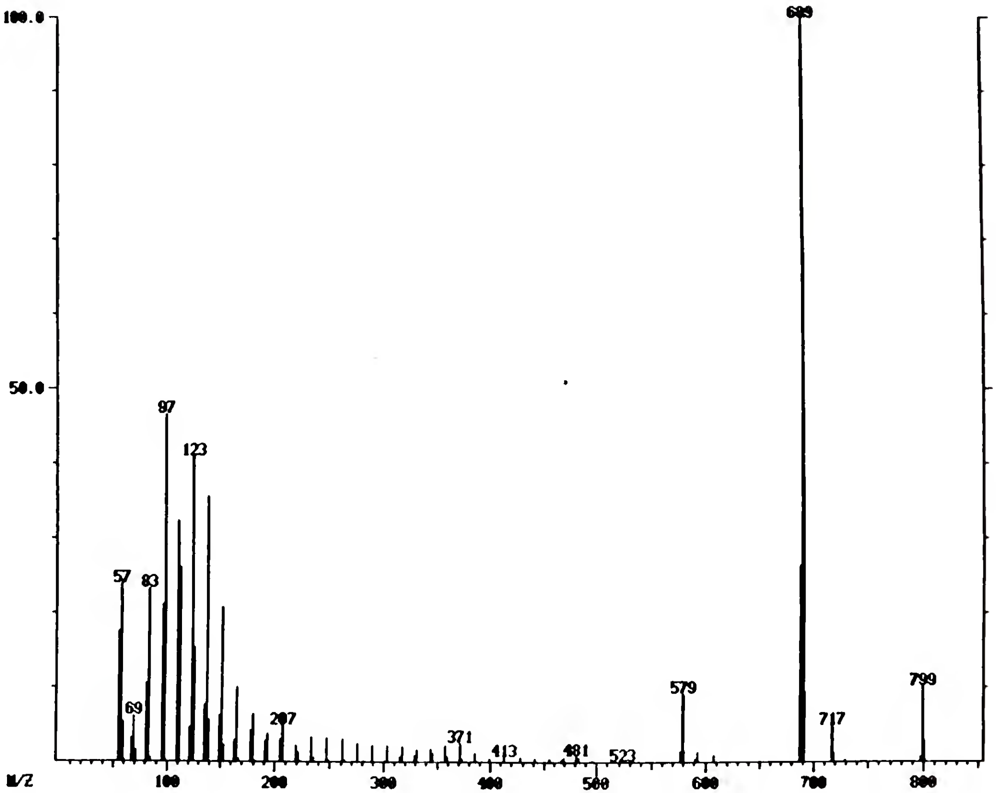
110 per linear repeating unit) and/or macrocyclic polyoctenamer (molecular weight 110 per cyclic repeating unit) are indicated by parent ion peaks at m/e = 221 and 331.

Mass spectrum of the second sample (Spectrum 4-8) exhibits parent ion peaks at m/e = 359, 469, 579, 689, 799, and 909, which are consistent with the presence of linear oligomers of the stoichiometry $(C_9H_{16})_2$ $(C_8H_{14})_x$ where x varies between 1 and 6. Parent ion peaks representative of a linear fraction and/or macrocyclic polyoctenamer were minute or absent for this sample.

While parent ion peaks are present that are consistent with linear oligomers of polyoctenamer, indicating that acyclic diene metathesis occurs in both reactions, these data alone do not eliminate the possibility of macrocycles of polyoctenamer being formed.

Another method to examine ring formation is to monitor the evolution of ethylene during the reaction. Ethylene forms only when ring closure occurs and not during ring opening polymerization. Thus, if ring closure is the only reaction taking place, no ethylene can be produced in later stages of the polymerization [101, 102 103 104, 105]. The detection of ethylene at late stages in the reaction and the formation of predominantly divinyl linear polymers indicates that acyclic diene metathesis occurs as opposed to ring opening metathesis polymerization, since both thermodynamics and kinetics limit the formation of rings at later stages of the reaction.

The acyclic diene metathesis polymerization of 1,5-hexadiene provides further evidence for the equilibrium step propagation, condensation polymerization nature of ADMET chemistry.



Spectrum 4-8. Chemical ionization mass spectrum of oligomers of polyoctenamer produced by ADMET polymerization of 1,9-decadiene.

The following chapter presents the polymerization of 1,5-hexadiene, elucidating its step propagation nature, the linearity of polymers produced and, the appropriate reaction conditions for ADMET polymerizations.

CHAPTER 5

THE STEP PROPAGATION, CONDENSATION NATURE OF ACYCLIC DIENE METATHESIS POLYMERIZATION

The acyclic diene metathesis reaction of 1,5-hexadiene (Figure 5-1) is described in this chapter and represents the step propagation, condensation type nature of the polymerization itself.

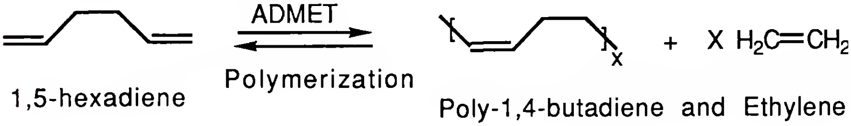


Figure 5-1. Acyclic Diene Metathesis of 1,5-Hexadiene

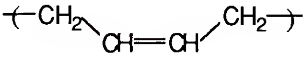
Vinyl addition side reactions previously prevented acyclic diene metathesis polymerization from producing high molecular weight polymers and had to be eliminated before acyclic diene metathesis polymerization could become a viable polymerization technique. The acyclic diene metathesis polymerization of 1,5-hexadiene was previously thought to be unlikely since side reactions dominated and could not be eliminated [56]. A challenge existed to produce perfectly linear, perfectly poly-1,4-butadiene from 1,5-hexadiene by acyclic diene metathesis polymerization techniques. The elimination of vinyl addition side reactions was investigated by determining whether any 1,2-vinyl linkages are present in the polybutadiene produced by ADMET polymerization of 1,5-hexadiene. The elimination of 1,2-vinyl linkages would result in the formation of perfectly linear, poly-1,4-butadiene.

Similar reaction conditions were used in the acyclic diene metathesis polymerization of 1,5-hexadiene as those employed in the polymerization of 1,9-decadiene. As a result, molecular weight comparisons were possible for the two different polymers formed under similar reaction conditions and by the same polymerization technique (ADMET) were possible.

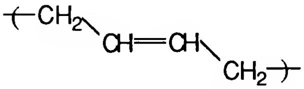
The absence of cyclization side reactions in acyclic diene metathesis polymerization is proposed to be a fundamental difference between acyclic diene metathesis polymerization and ring opening metathesis polymerization. Also, the polydispersities of poly-1,4-butadiene formed by acyclic diene metathesis polymerization of 1,5-hexadiene could verifies the assumption that acyclic diene metathesis is an step propagation type polymerization reaction. Further, the mass spectroscopy data of the polymer and gasses produced, elucidates the condensation nature of ADMET polymerizations. The results of these investigations are reported in this chapter, specifically addressing the step propagation, condensation nature of ADMET polymerizations.

Determining the Linearity of Acyclic Diene Metathesis Produced Polybutadiene.

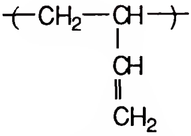
Traditionally, polybutadiene has been produced by one of several different chain polymerization methods [5]. The monomer used in these chain polymerizations is 1,3-butadiene, a conjugated diene capable of undergoing both 1,2- and 1,4-addition reactions [106], and the polymers that result consist of a combination of three possible repeat units (Figure 5-2).



cis 1,4-olefin
repeat unit



trans 1,4-olefin
repeat unit



1,2-vinyl
repeat unit

Figure 5-2. The Three Possible Repeat Units of Polybutadiene.

The physical properties of a polybutadiene sample depend on the ratio and distribution of these repeat units, and consequently, research has been conducted in order to control the number and type of repeat units present and ultimately produce stereochemically pure polymers. While the relative amount of each repeat unit present is dependent on the reaction conditions and polymerization technique used, the mechanism of any conjugated vinyl addition, chain polymerization suggests that all three of the possible repeat units should be present, at least to some degree (Figure 5-3).

It is debatable whether perfectly linear, poly-1,4-butadiene has ever been produced, though researchers have reported that samples without the presence of 1,2-vinyl linkages have been made [107]. Although employing certain reaction conditions can minimize the formation of 1,2-vinyl linkages in a polybutadiene sample, the mechanism by which these reactions proceed presents the possibility for 1,2 addition, as shown in Figure 5-3, for anionic chain polymerization.

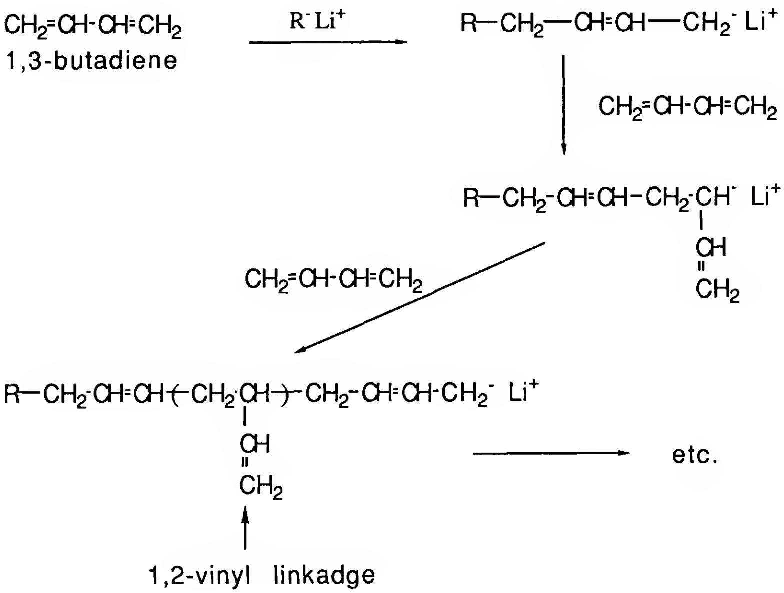


Figure 5-3. Polybutadiene formed by anionic polymerization, indicating the formation of a 1,2-vinyl linkage via a 1,2-addition reaction.

Generally, organolithium initiation in hydrocarbon solvents yields polybutadiene containing 48-58% trans 1,4-olefin, 33-65% cis 1,4-olefin, and 7-10% 1,2-vinyl repeat units [107]. If THF is used as solvent, the polymer that is produced contains 87% 1,2-vinyl repeat units. Numerous other initiators and solvent systems exist and the percentage of 1,2-vinyl units can be minimized [108] .

In contrast to this situation, acyclic diene metathesis polymerization proceeds via a polymerization mechanism that completely eliminates the possibility of forming 1,2-vinyl repeat units, and thus, 1,5-hexadiene produces poly-1,4-butadiene without the presence of poly-1,2-butadiene. The reaction conditions are presented in Figure 5-4, and the mechanism for this reaction is shown in Figure 5-5 (Page 135).

$CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH_2$
1,5-hexadiene

$$\Bigg\downarrow \begin{array}{l} \text{Catalyst : Monomer} \\ \quad\;\, 1 \quad\;\; : \;\; 5000 \\ \text{Vacuum } (10^{-6}\text{mm Hg}) \\ \text{Heat } (25\text{-}55°\text{C}) \end{array}$$

$$-\!\!\left(CH{=}CH{-}(CH_2)_2 \right)\!\!-_{n} \qquad + \qquad n\, CH_2{=}CH_2$$

Perfectly Linear,
Perfectly, Poly-1,4-butadiene

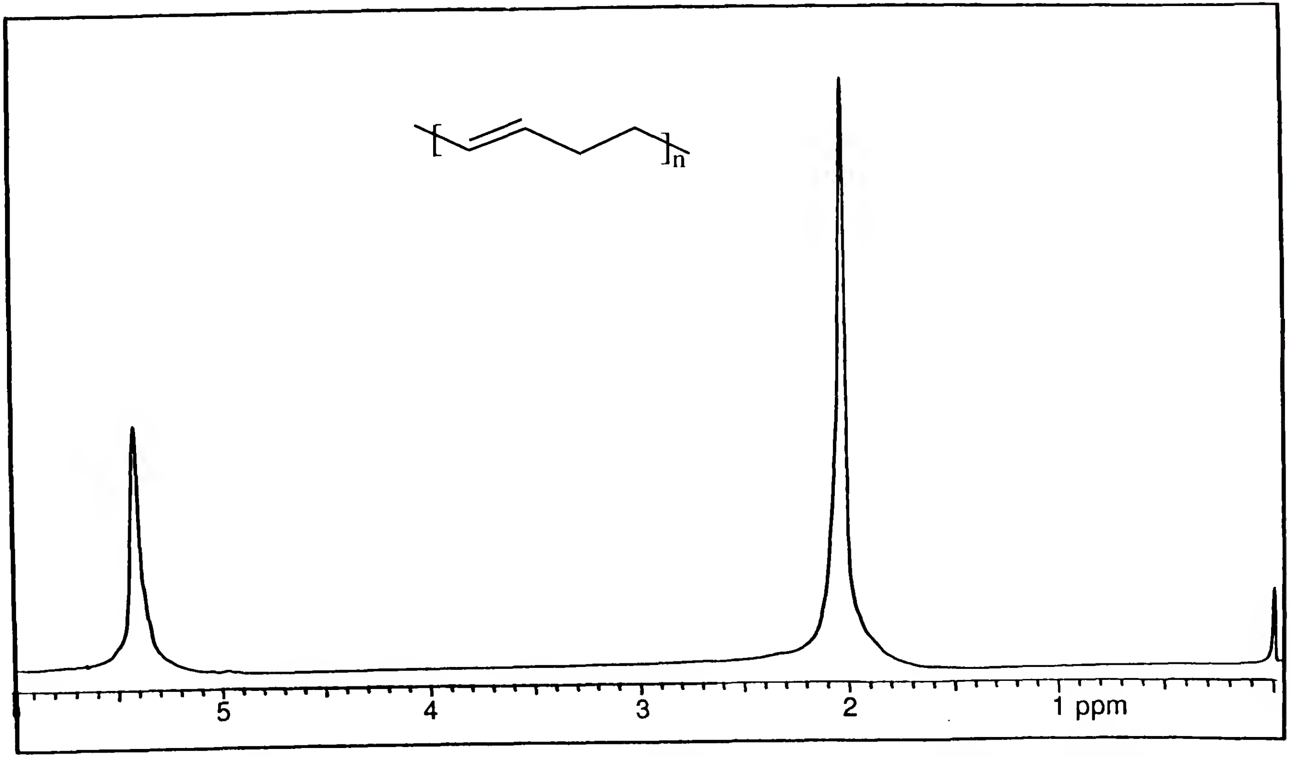
Figure 5-4. Acyclic Diene Metathesis Polymerization of 1,5-Hexadiene Producing Perfectly Linear, Poly-1,4-butadiene.

Three methods were used to probe for the presence of a 1,2-vinyl linkage: proton NMR, carbon NMR, and infrared spectroscopy.

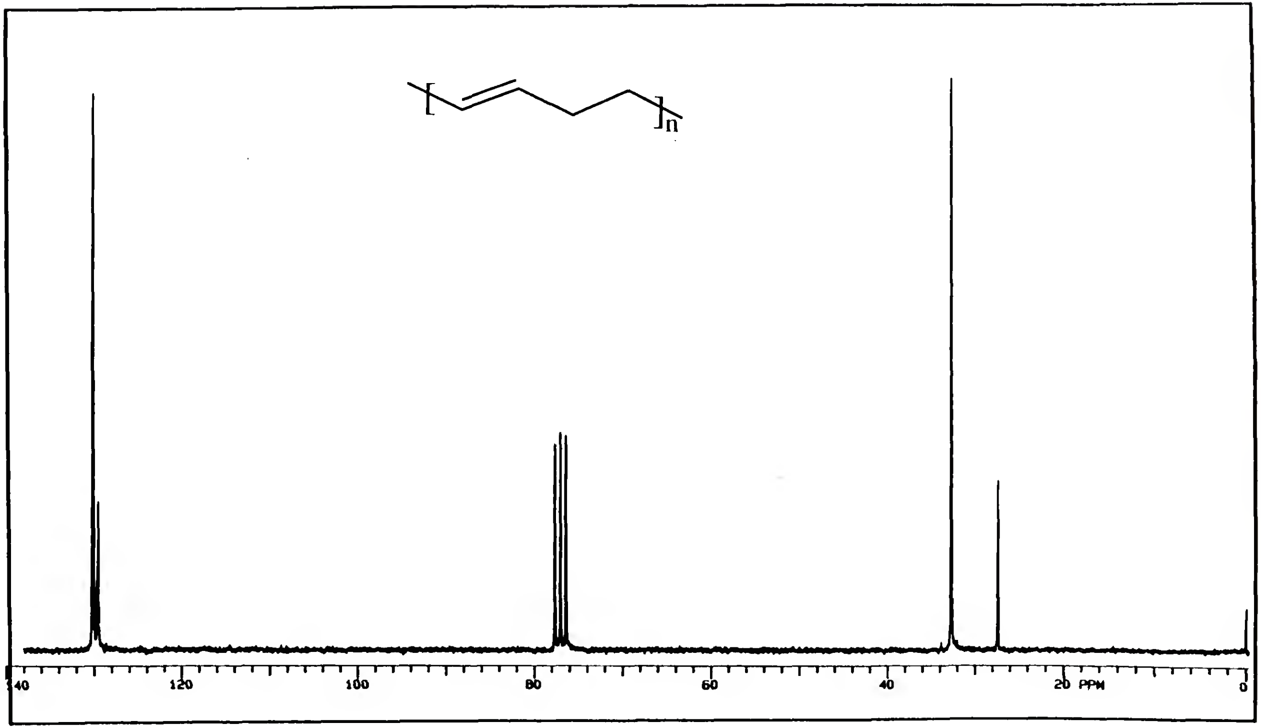
The proton NMR spectrum of the product formed from the acyclic diene metathesis polymerization of 1,5-hexadiene (Spectrum 5-1) confirms the presence of perfectly linear poly-1,4-butadiene with no branching being observed [109]. All signals result from the two sets of protons present in the repeating unit. A singlet at 5.42 ppm corresponds to the internal olefinic protons and another singlet at 2.05 ppm corresponds to the four methylene protons present in the repeating unit. These proton NMR results show that side reactions, such as 1,2-vinyl addition, do not occur.

Markedly absent in the ^{13}C NMR spectra (Spectrum 5-2) are resonances due to 1,2-1,4 linkages which are evident in polymers produced by chain polymerization techniques. The methylene carbon resonances of a 1,2-1,4 linkage are found at 30.9, 35.0, and 39.1 ppm [110]. Numerous other signals are possible due to the stereochemical environment surrounding the 1,2-1,4 linkage. None of these peaks were observed in 1,4-polybutadiene produced by ADMET.

Only two signals were observed in the methylene region of the ^{13}C NMR (i.e. a cis-cis resonance at 27.5 ppm and a trans-trans resonance at 32.7 ppm. The methylene resonances resulting between a cis-trans configuration is reported to resonate at 26.44 and 32.88 ppm in model compounds [111]. These resonances were indistinguishable from the cis-cis and trans-trans signals in the polymer samples produced by ADMET.



Spectrum 5-1. 200 MHz ^1H NMR of linear 1,4-polybutadiene produced by ADMET polymerization of 1,5-hexadiene.

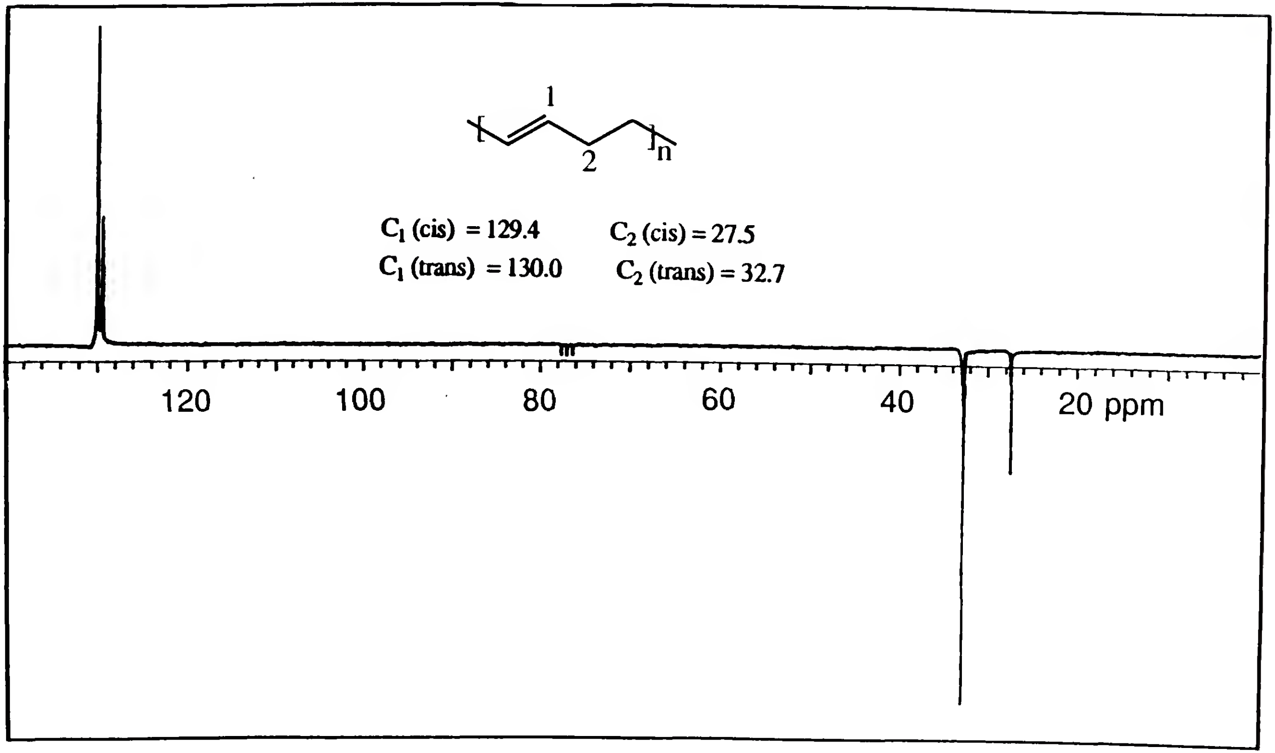


Spectrum 5-2. 50 MHz ^{13}C NMR of linear 1,4-polybutadiene produced by ADMET polymerization of 1,5-hexadiene.

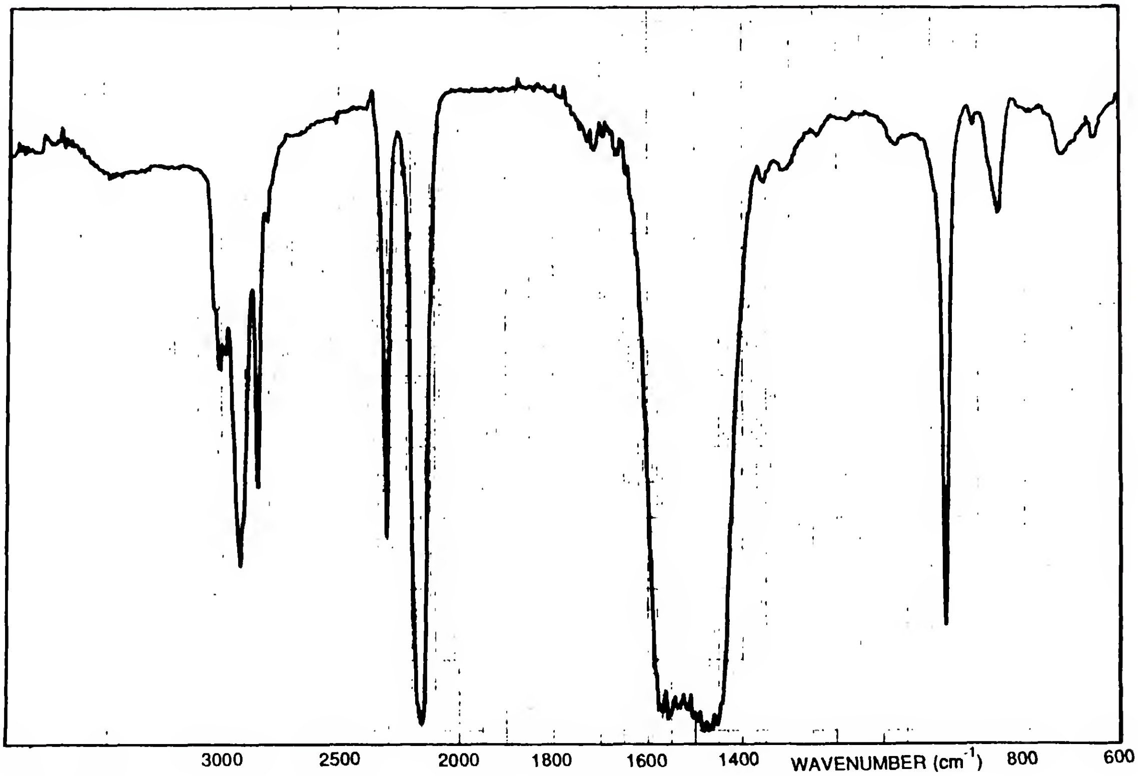
Proton decoupled, quantitative ^{13}C spectra, of the olefinic region confirms the absence of any 1,2-vinyl unit resonances between 110 and 150 ppm [110, 112]. Only two resonances corresponding to a cis-cis linkage at 129.4 ppm and a trans-trans linkage at 130.0 ppm are observed in the olefinic carbon region

An attached proton carbon NMR (APT) spectrum (Spectrum 5-3) of the product formed under bulk reaction conditions also indicates the absence of 1,2-vinyl units. An APT carbon NMR clearly delineates between methine and methylene carbon atoms, and Spectrum 5-3 indicates that no vinyl methylene resonances are found between 110 and 150 ppm nor were methine resonances observed in the region 20-45 ppm. The absence of any ^{13}C resonances, resulting from the presence of a 1,2 linkage, provides further evidence that perfectly linear, poly-1,4-butadiene is produced.

Infrared absorption spectra of the poly-1,4-butadiene product also support this conclusion. A minute absorption at 910 cm^{-1} can be attributed to the vinyl end groups of the polybutadiene sample of lower molecular weight and not to the presence of 1,2-vinyl repeat units (Spectrum 5-4). Vinyl endgroups also are observed in the NMR spectra of a low molecular weight sample and substantiate this assignment. The predominate absorption at 970 cm^{-1} results from a large concentration of trans 1,4-olefin repeating units [110, 113]. A much smaller absorption band is observed in the cis 1,4-olefin absorption region, ranging from 700-850 cm^{-1}. The cis band has been reported to be sensitive to its environment [113, 114], and a sharp peak is observed at 850 cm^{-1} indicating a consistent



Spectrum 5-3. 50 MHz ^{13}C NMR (attached proton test) of linear 1,4-polybutadiene produced by ADMET polymerization of 1,5-hexadiene.



Spectrum 5-4. Infrared spectrum of linear 1,4-polybutadiene produced by ADMET polymerization of 1,5-hexadiene.

environment surrounding the cis 1,4-olefin units, which indicates that no absorptions due to cis 1,4-1,2 linkages are present.

The absence of poly-1,2-butadiene in acyclic diene metathesis polymerization can be explained mechanistically. As illustrated in Figure 5-5, the formation of 1,2-vinyl linkages, under acyclic diene metathesis conditions, is impossible. The polymerization mechanism shows that if an internal olefin unit reacts with catalyst (reverse of steps 4 and 3), only monomer (or oligomers) and a new metal carbene will result. Only the reaction of vinyl units results in productive acyclic diene metathesis polymerization and an increase in molecular weight. Thus, acyclic diene metathesis polymerization is the first synthetic route that mechanistically eliminates the possibility of any 1,2-vinyl repeat units and produces linear poly-1,4-butadiene.

Determining Optimal Reaction Conditions for Acyclic Diene Metathesis Polymerizations

Polyoctenamer polymerization experiments have shown that large volumes of solvent produce low molecular weight polymers and that magnetically agitated bulk reactions are limited to producing polymers with molecular weights in the 10^4 range. In order to compare the results obtained in the synthesis of polyoctenamer, 1,5-hexadiene polymerizations were performed using reaction procedures similar to that used for 1,9-decadiene acyclic diene metathesis polymerizations.

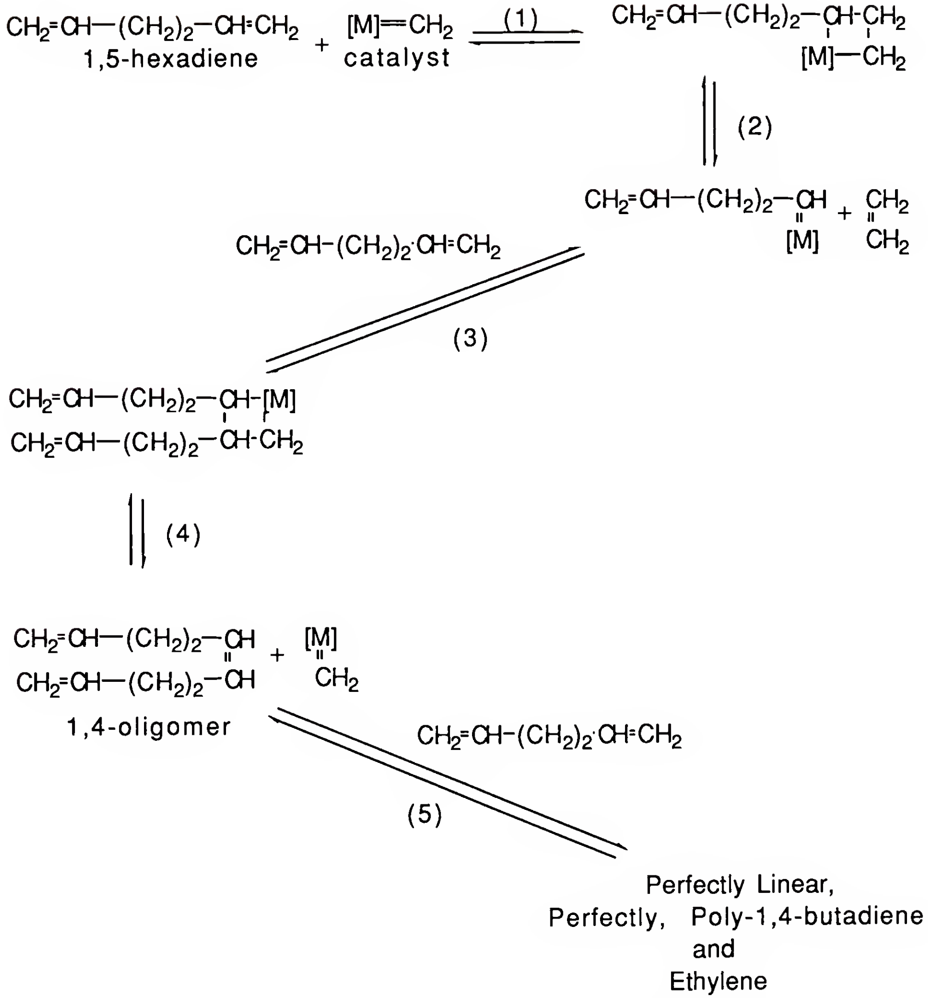


Figure 5-5. Mechanism for Acyclic Diene Metathesis Polymerization of 1,5-hexadiene.

Large Volume of Solvent

The first reaction was performed using a large volume (100 mL) of toluene as solvent. A reaction temperature of approximately 25°C was maintained while a partial vacuum (10^{-4} mmHg) was applied at 24 hour intervals in order to remove the ethylene produced.

The reaction was allowed to continue for a long period of time, in the expectation that equilibrium conditions would be achieved and a polymer with a polyuniformity of approximately 2 would result. The molecular weight of polybutadiene formed can be compared to the polyoctenamer sample formed under similar reaction conditions.

Molecular weights were obtained by size exclusion chromatography, and polybutadiene formed when large volumes of solvent and long reaction times were used, exhibits a $\overline{Mw}$ of 1.64×10^4 and an $\overline{Mn}$ of 8.3×10^3 (Figure 5-6). The uniformity of the sample is 1.98, exactly as predicted for an equilibrium step propagation condensation type polymerization.

These results confirm that if large volumes of solvent are used in acyclic diene metathesis polymerizations (ie., dilution of functionality reduces reaction rates) low molecular weights result. Polyoctenamer samples formed under similar conditions had comparably low molecular weights.

Reasons why the use of large volumes of solvent in acyclic diene metathesis polymerizations result in low molecular weight polymers are hypothesized. A large volume of solvent causes cooling of the reaction section of the apparatus because cold solvent

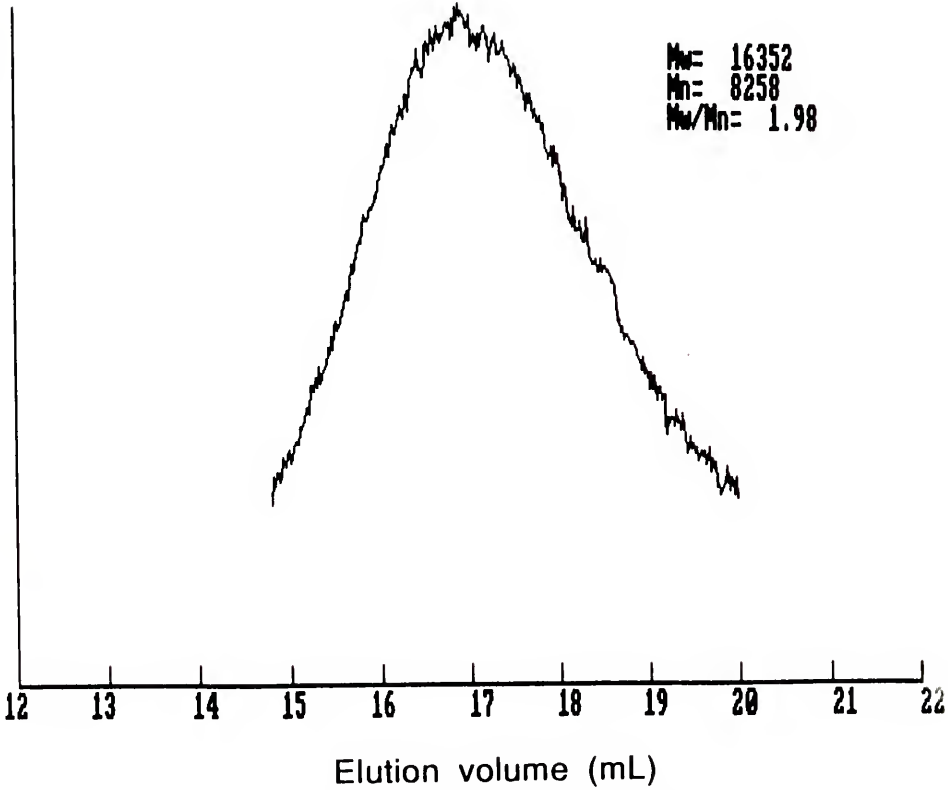


Figure 5-6. Size exclusion chromatography curve of linear 1,4-polybutadiene produced by ADMET polymerization of 1,5-hexadiene.

(approximately -60°C) is constantly returned into the reaction section of the apparatus by the condenser. Thus, the reaction temperature is lowered below the desired 50-55°C range, and allows precipitation of the polymer on the sides of the reaction vessel.

Polymer that had precipitated on the sides of the reaction vessel was no longer in contact effectively with the catalyst; rendering it inaccessible to acyclic diene metathesis polymerization. The main driving force behind acyclic diene metathesis polymerizations is the efficient removal of ethylene. The return of solvent and monomer into the reaction section from the gas trap prevented efficient removal of ethylene and results in slower reactions. The formation of low molecular weight polymer by ADMET polymerization is attributed to reaction conditions employed and not an inefficient chemical reaction.

Bulk polymerization conditions

Under bulk reaction conditions a polymerization was performed under bulk reaction conditions and the reaction temperature was increased from 25°C to 55°C. A total reaction time of 10 hours was chosen in order to compare the molecular weight of the polymer formed with the polyoctenamer formed under similar reaction conditions.

The product formed under bulk reaction conditions, had a $\overline{Mw} = 2.8 \times 10^4$ and a $\overline{Mn} = 1.4 \times 10^4$, corresponding to a dispersity of 2.05 (Figure 5-7). Under magnetic agitation and bulk reaction conditions, acyclic diene metathesis polymerizations were limited to the 10^4 molecular weight range. Both polyoctenamer and

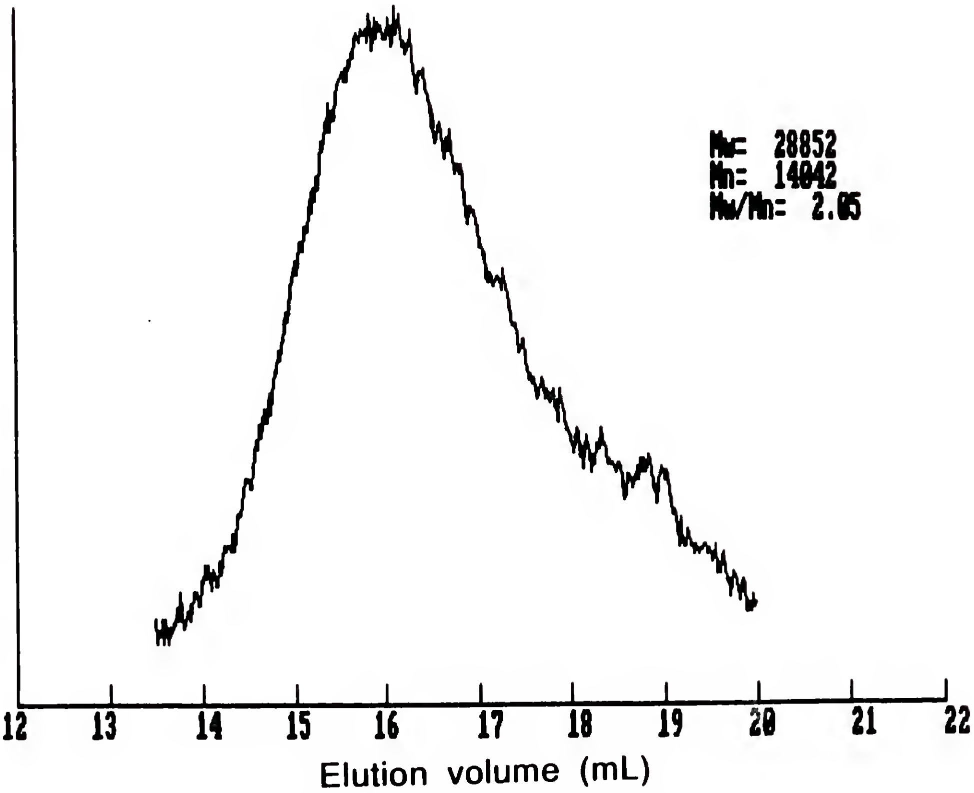


Figure 5-7. Size exclusion chromatography curve of linear 1,4-polybutadiene produced by ADMET polymerization of 1,5-hexadiene.

poly-1,4-butadiene had viscosities that prevented magnetic agitation at 50°C, once the polymer reached the 10^4 molecular weight range. High torque stirring devices will overcome the problem of agitation and acyclic diene metathesis polymerizations will produce higher molecular weight polymers under bulk conditions if agitated effectively.

An Evaluation of the Equilibrium Step Propagation Condensation Nature of Acyclic Diene Metathesis Polymerizations.

Chapter 1 gives a detailed discussion of the differences between ring opening metathesis polymerization (chain propagation) and ADMET polymerization (step propagation) mechanisms and Figure 5-8 illustrates the chemistry under consideration. The following results confirm the assumption that ADMET proceeds by a step propagation condensation mechanism.

Size exclusion chromatography data can be used to distinguish between polymers formed by step or chain polymerization mechanisms. The polydispersities of the poly-1,4-butadiene samples produced from the polymerization of 1,5-hexadiene by acyclic diene metathesis polymerization confirm that acyclic diene metathesis polymerization proceeds by a step growth polymerization mechanism. Polydispersities of 1.98 and 2.05 are observed for the two poly-1,4-butadiene samples prepared; thus, indicating that acyclic diene metathesis polymerization is an equilibrium step propagation condensation type reaction.

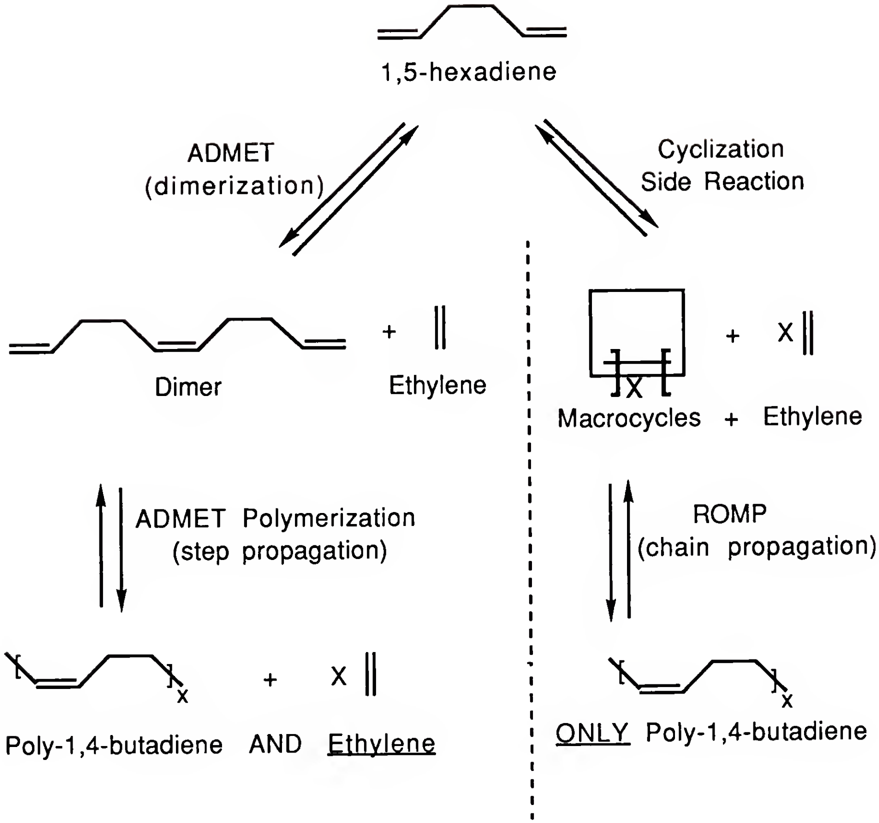
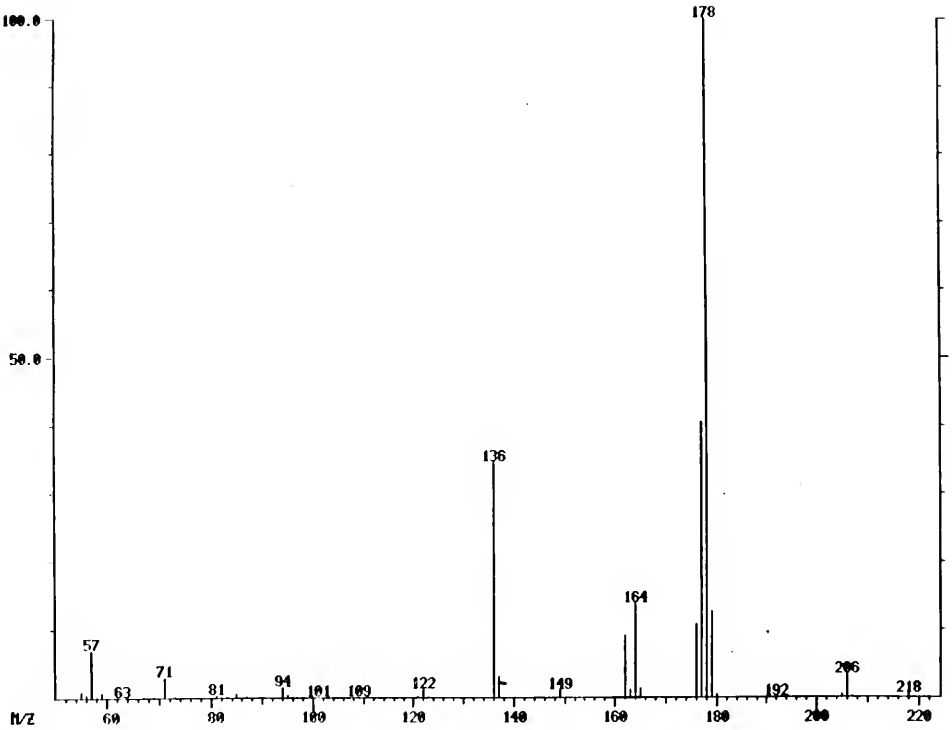


Figure 5-8. Acyclic diene metathesis of 1,5-hexadiene.

Polydispersities approaching 2.0 are in contrast to ring opening metathesis polymerizations [34, 42] which have been shown to be living polymerizations occurring by a chain growth mechanism, which produces polyuniformities approaching unity.

The step propagation nature of ADMET can be confirmed by detecting linear polymer with vinyl endgroup. Mass spectroscopy is a technique which identifies molecules through their parent ion peaks and was used to detect linear polybutadiene and polyoctenamer. Observing parent ion peaks that result from macrocyclic compounds or linear fraction of polyoctenamer in the acyclic diene metathesis polymerization of 1,9-decadiene might indicate that acyclic diene metathesis is cyclizing 1,9-decadiene. If so, cyclooctene and larger cyclo-olefins might be polymerized by ring opening metathesis polymerization chemistry implying that acyclic diene metathesis is limited to small molecule synthesis and, thus is not a true polymerization reaction. Oligomeric poly-1,4-butadiene was analyzed by chemical ionization mass spectroscopy to determine the dominant reaction mechanism of acyclic diene metathesis polymerization.

Mass spectroscopy shows that acyclic diene metathesis polymerization is the dominant reaction. While parent ion peaks are present that correspond to either fractions of linear poly-1,4-butadiene or macrocyclic polybutadiene, the majority of the parent ion peaks correspond to linear poly-1,4-butadiene fractions and contained vinyl endgroups. The three m/e dominant peaks (Spectrum 5-5) at 136, 164, and 178 result from fractionation of a trimer (m+=192) of butadiene. Cyclization of 1,5-hexadiene to macrocyclic polybutadiene cannot be ruled out however, apparently it is not the principle reaction occurring under the experimental conditions employed. If present, macrocycles are in low concentrations and ring opening metathesis polymerization is insignificant and does not



Spectrum 5-5. Chemical ionization mass spectrum of linear 1,4-polybutadiene produced by ADMET polymerization of 1,5-hexadiene.

effect the polydispersities of polymers produced by acyclic diene metathesis polymerization of 1,5-hexadiene.

The step propagation and also the condensation nature of ADMET polymerization is further demonstrated by the formation of ethylene (Figure 5-8). The production of ethylene throughout the duration of acyclic diene metathesis polymerization confirms that ADMET is a condensation type reaction. Ring opening metathesis polymerization does not produce ethylene. If the 1,5-hexadiene had been cyclized initially into macrocycles no ethylene would be produced during the later stages of the polymerization .Thus, the continious formation of ethylene confirms the dominance of acyclic diene metathesis polymerization.

In light of the reactions reported herein, high molecular weight poly-1,4-butadiene can be synthesized from 1,5-hexadiene by an equilibrium step propagation condensation type polymerization. Acyclic diene metathesis (ADMET) polymerization of 1,5-hexadiene produces perfectly linear, poly-1,4-butadiene without a trace of any side reactions. Side reactions that previously limited acyclic diene metathesis polymerizations to the formation of oligomers and undesirable, intractable products [58] have been successfully eliminated, and the first synthetic route by which 1,2-vinyl repeating units can be completely eliminated in the formation of polybutadiene has been described.

The optimum reaction conditions have by no means been found, but bulk reactions with mechanical stirring seem to be the most promising. The development of new catalysts and more effective reaction conditions is yet another challenge that awaits the acyclic diene metathesis polymerization chemist.

The number of new and exciting polymers that can now be synthesized by means of acyclic diene metathesis polymerizations are endless. As a result, a new field for the imagination and creativity of the polymer chemist has opened.

Ring opening metathesis polymerization is no longer the only metathesis polymerization reaction. It is firmly believed that acyclic diene metathesis polymerization will prove to be a worthy bearer of the olefin metathesis family name.

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BIOGRAPHICAL SKETCH

Jan Geldenhuys Nel was born on a bright and sunny 12th of November, 1960, in Port Elizabeth, South Africa. His early years were spent on the family farm learning the fundamentals of life.

In December of 1978, he graduated from high school, obtaining a cumulative A aggregate on the state wide matriculation examinations. After 3 years he received his B.S. in chemistry and physics at the University of Port Elizabeth. A year later he obtained his B.S. Honors degree and proceeded to do a masters degree in inorganic chemistry at the University of Port Elizabeth.

The opportunity to study chemistry in the USA was a challenge that could not be rejected. Subsequently, Jan arrived in Gainesville on a hottest of May, 1985.

An exciting and enlightening 4 years were spent doing research under Dr. Ken "Don't Give Up" Wagener. Time will tell what the future holds, in God we trust!

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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